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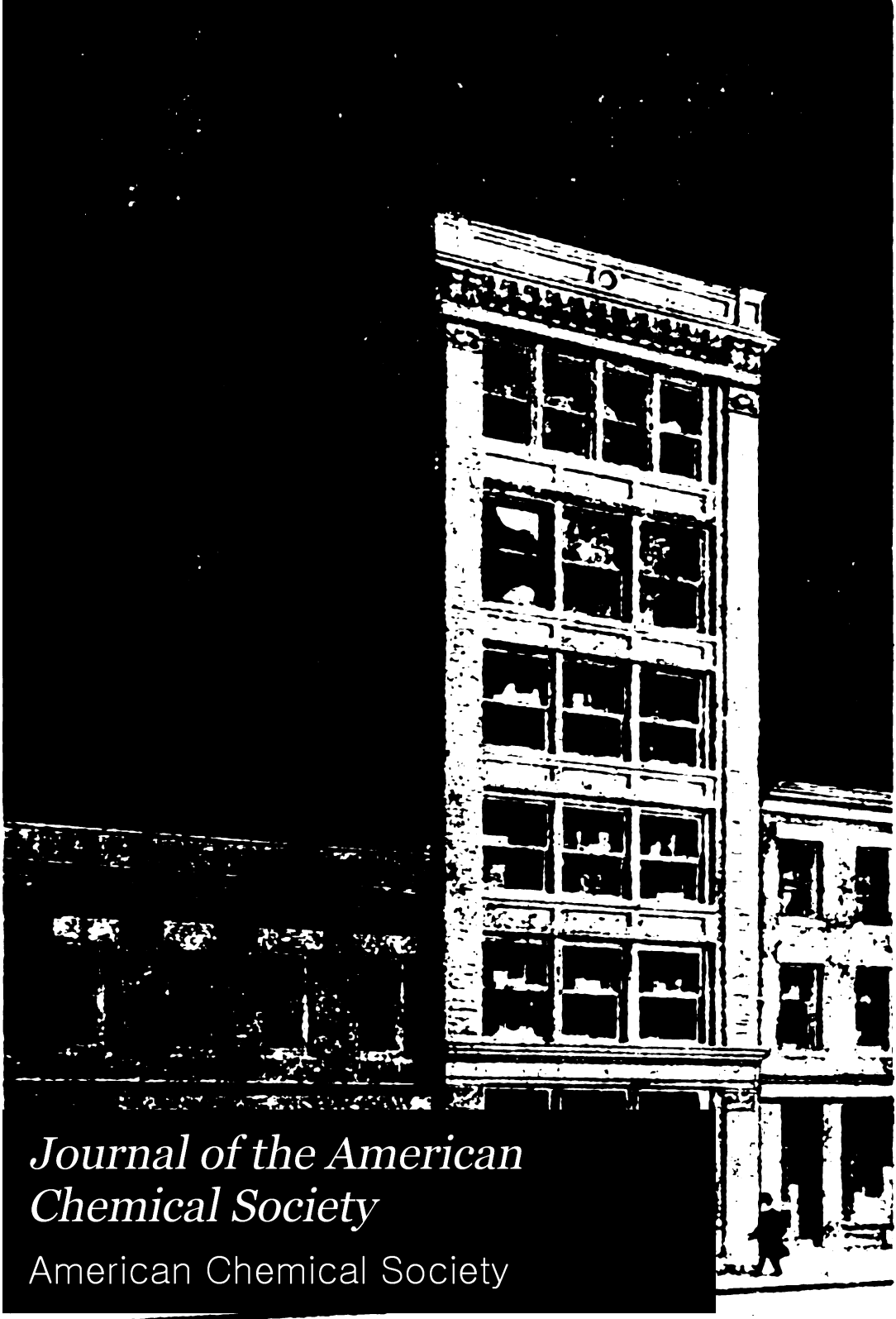
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GASES VS. SOLIDS: AN INVESTIGATION OF THE INJURIOUS INGREDIENTS OF SMELTER SMOKE.

BY W. CLARENCE EBAUGH.

Received February 4, 1907.

Probably the most important question confronting metallurgists and smelter men today is that of the effect of "smelter smoke" upon vegetation. During the last five or ten years there has been not only a marked increase in the number of damage suits brought against smelting companies, but, what is far more serious, suits for temporary or permanent injunctions have been begun. In some instances the latter suits have been decided in favor of the complainants. Three well known cases may be cited: (a) United States *vs.* Mountain Copper Company, whose plant is near Redding, Shasta County, California, (b) an association of about four hundred and fifty farmers in the Salt Lake valley against four smelters operating at Murray and Bingham Junction, Utah, and (c) the Deer Lodge Valley Association of farmers against the Anaconda Copper Mining Company, of Anaconda, Montana. In the first two instances judgement was rendered in favor of the complainants, and in the last mentioned the legal battle has not been concluded (January, 1907). The questions suggested by the title of this paper are of great moment in courts of law trying such cases. Moreover a complete understanding as to the relative amounts of damage caused by sulphur dioxide and solid emanations from lead and copper smelters would be of the highest value in determining the location of a smelter, the construction of its flue system and the disposition of its volatile waste products. The botanist and the practical agriculturalist are equally interested in the question.

A perusal of the literature bearing upon the smelter smoke problem shows that the view generally accepted is that the gas sulphur dioxide is responsible for the damage to vegetation, and the "fume" or finely divided solid emanation, containing arsenic, lead and copper, causes sick-

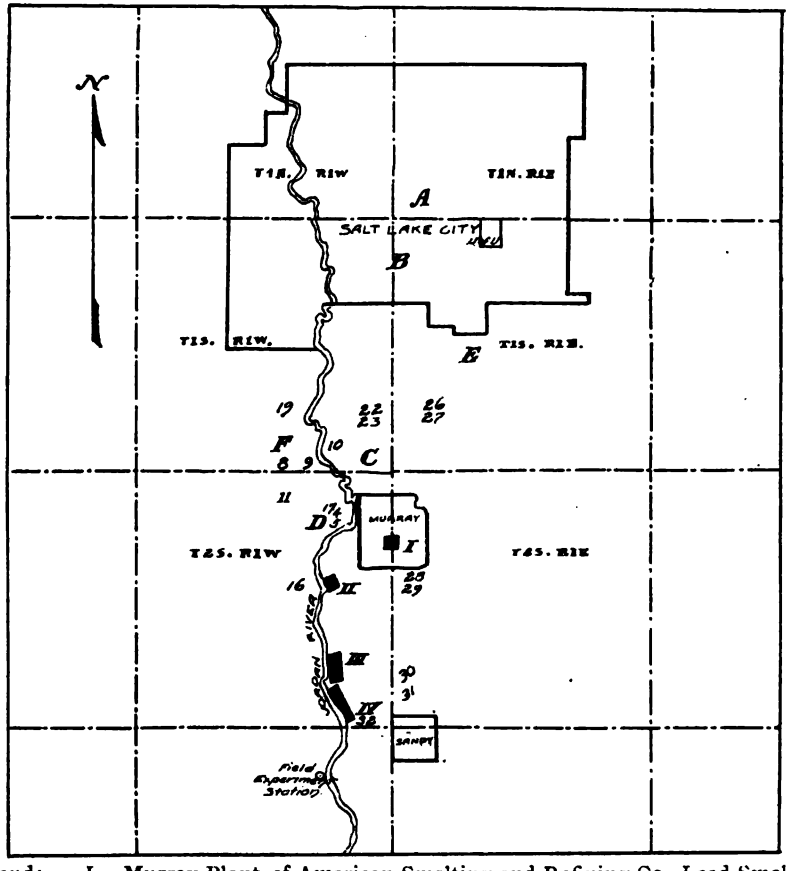
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ness and death of animals.[1] For a long time the author's view coincided with the one just given, but as the result of a large amount of experimental work carried out by him he is now persuaded that undue emphasis has been laid upon the injurious effect of sulphur dioxide upon growing field plants, and that the harmful action of the solid emanations from the smelters, the so-called "flue dust," has been seriously underestimated.

Several facts should be noticed in connection with the damage sustained

FIG. I.

Map showing locations of (a) Smelters, (b) Aspirator Stations, (c) Field Experiment Station, (d) places where samples were collected.



Legend: I. Murray Plant of American Smelting and Refining Co. Lead Smelter.
II. Copper Smelter of Utah Consolidated Mining Co., Highland bog Plant.
III. Copper Smelter of Bingham Consolidated Mining and Smelting Co.
IV. Copper and Lead Smelters of United States Mining Company. A, B, C, D, E, F—Aspirator Stations.

[1] Haselhoff and Lindau "Rauchbeschädigung," Gebrüder Bornträger, Leipzig. Haywood, "Injury to Vegetation by Smelter Fumes," Bull. 89, Bureau of Chemistry, U. S. Dept. of Agriculture.

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by vegetation in the Salt Lake valley. In the first place the injury does not occur simultaneously over a large area; on the contrary it seems to be restricted in its range. Secondly, it is rarely found that a number of crops grown successively in a given locality show the effect of smoke. Finally, the blighting action of the smoke is observed at its maximum during wet weather and at its minimum when the atmosphere is dry. The result is that one seldom finds a farmer complaining about a total loss of crops, and it is this element of partial loss, varying from year to year, that makes the legal question of damages hard to decide.

Thinking that it might be of interest to know the average amount of sulphur dioxide in the atmosphere of this section of the country, a series of experiments was carried out by the author in the early part of 1905. A number of students from the Department of Chemistry consented to act as observers and were placed in charge of stations distributed over the northern part of the valley. No students from the section of the country lying south, east and west of the smelters went to and from their homes daily, consequently no stations could be established there, desirable though they would have been. The situation of the smelters, stations and other points to be referred to later can be learned from the accompanying map (Figure 1).

Each station was provided with an aspirator and absorption bottle. Known volumes of air, approximately twenty liters each, were drawn through solutions of iodine, and later these solutions were analyzed for their sulphuric acid content by the ordinary gravimetric method. An approximate calculation as to the amount of sulphur dioxide by volume in a million parts of air could then be made. A summary of the results is shown in Table 1. It may be said that a second series of determinations carried out in the autumn of 1905 corroborated the results here given, although carboys were used as aspirators, two absorption bottles in train were employed, and forty liter samples of air were analyzed.

TABLE I.

Summary of results of analyses made to determine the average sulphur dioxide content of the atmosphere in the Salt Lake Valley.

Parts SO_2 Per million.		Stations A	B	C	D	E	F	Total	Per cent. of Total
0	Number of Analyses	89	38	98	53	28	5	311	59.35
1		20	12	10	13	2	3	60	11.45
2–3		32	11	32	16	12	2	105	20.04
4–6		10	3	14	6	1		34	6.50
7–10		1	1	3	3		2	10	1.91
Over 10				4				4	0.76
Total		152	65	161	91	43	12	524	

So far as the practical value of these results is concerned it must be admitted that they do not carry much weight. Air charged with enough sulphur dioxide to do damage to plants might be present for ten, twenty

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or thirty minutes, but when this quantity is averaged over a twelve or twenty-four hour period it makes the result appear so insignificantly small as to be almost negligible. Nevertheless the very small amount of sulphur dioxide found is certainly surprising.

It would be very desirable to have a method of analysis that would enable one to determine with accuracy the amount of sulphur dioxide in the atmosphere at a given time and and place, not an average over a long period, but such a method is unknown to the author.

A rough estimate as to an upper limit of the sulphur dioxide content of the air at a given distance from the smelter can be made if (a) the size of the stacks, (b) sulphur dioxide content of the stack gases, (c) width and thickness of the visible smoke column at a given time and place, be known. Measurement of the combined smoke columns coming from a group of smelters at a distance of a mile from the nearest one, showed the width to vary from one to three thousand feet according to the atmospheric conditions. Granting that the sulphur dioxide did not exceed one and a half per cent by volume in the gases as they issued from the stacks, that the smoke column became at least one third as thick as it was broad, and that the combined areas of the stacks in question was known, it could be shown by proportion that the possible sulphur dioxide content would not exceed one part in forty or fifty thousand at the place mentioned. Diffusion, however, would surely tend to make the possible content still lower.[1]

Probably the best summary of the effects of sulphur oxides upon plants is that given by Haselhoff and Lindau.[2] The authors are well known botanists and chemists, and their compilation of the work of others and their original contributions to the knowledge of the subject in hand show characteristic German thoroughness. In effect they say:

"1. Even after severe and oft-repeated action upon the soil of the sulphurous and sulphuric acid contained in smoke, whether the action be direct or by means of atmospheric precipitation, an essential increase in the sulphuric acid content of the ground does not take place. Apart from a transposition of the constituents of the soil no change in its composition occurs, and therefore one can scarcely tell whether an injury to the soil has been caused by the sulphurous and sulphuric acid gases in the smoke.

"2. The direct action of free (uncombined) sulphurous or sulphuric

[1] Analyses made by the writer have shown that the sulphur dioxide content of the gases in the various lead stacks varies from 0.20 to 0.50% by volume, gases in copper stacks (blast furnace and roaster) from 0.90 to 2.50 %, and gases in converter stacks from 0.20 to 1.20 %. In reverberatory stacks the quantity of sulphur dioxide is negligibly small—0.01 % or less.

[2] Loc. cit., pp. 143-145.

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acid of smoke upon the roots of plants is improbable under the ordinary conditions of agriculture and forestry. Should an increase in the sulphate content of the soil take place, through the action of the sulphurous and sulphuric acid gases in the smoke, it is without influence upon the growth of plants; therefore an injury to vegetation by acid smoke gases acting by means of the soil is as good as excluded.

"3. An injurious effect from acid smoke gases acting upon plants can only take place if the said gases come directly in contact with the leaf organs of the plant.

With damage to vegetation by these acids there always goes parallel increase in the sulphuric acid content. The latter shows itself also in uninjured plants grown upon a soil rich in sulphates, and therefore a high sulphate content cannot always be accepted as proof of damage by smoke. Far more important in this connection are the conditions of the locality in which the plants were grown.

"4. The sensitiveness of plants toward sulphuric and sulphurous acid varies; even plants of the same kind are more or less sensitive according to their individual idiosyncrasies.

"5. The long continued action of sulphurous acid, even in quantities as small as one part per million, has proved hurtful to plant growth. According to the experiments of M. Freytag sulphuric acid proved to be the more injurious, and according to the experiments of J. von Schroeder, less injurious, than sulphurous acid.

"6. The masses of sulphurous acid taken up by equal leaf surfaces of two different plants under like conditions and in the same time, do not give a measure of the damage which the plants have suffered; on the contrary the specific peculiarities in the make-up of the individual plants must be taken into account.

"7. Fissure openings of the leaf organs play no role in the absorption of sulphurous acid; the gas is taken up principally by the whole leaf surface, and not by fissures. Therefore the difference in the amounts of sulphurous acid that penetrates into the leaf is not to be explained by the number of fissures, but by other conditions dependent upon the organization of the individual plants.

"8. The effect of sulphurous acid is to cause a derangement of the water circulation, which is made manifest by an increased loss of water and leads to the drying out of the leaves.

"9. The absorption of sulphurous acid,—and accordingly the destruction of the water circulation,—is greater for a given quantity of sulphurous acid in the same time in the presence of light, at a high temperature and in dry air, than in the dark, at a lower temperature and in damp air; consequently sulphurous acid and the acid smoke gases are generally more injurious by day than by night.

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"10. Morphologically the effect of sulphurous acid shows itself in the formation of spots on leaves, the dying off of leaves and twigs, the "falling behind" of the yearly growth in thickness, and finally the death of the plant.

"11. In the interior of the plant cells plasmolysis is developed, the chlorophyl grains die and finally form with the plasma and the other contents a brown amorphous mass. At the same time the tannin usually separates, especially where the injury has come about gradually, and can be recognized by the brown or black nuclei ("Zusammenballungen") in the cells.

"12. We have represented the sulphurous acid as destroying the life of the plasma in the cell. Probably it acts as sulphuric acid, which is formed by the oxidation of the sulphurous acid with the oxygen of the assimilating chlorophyl grains, in the presence of water derived from the cell sap.

"13. By the continuous action of water, as for example rain, the absorbed sulphurous or sulphuric acid in the dead leaf organ can be separated again. In the case of conifers, and probably also in other plants whose leaves are resinous or waxy, the sulphurous or sulphuric acid content, absorbed from the smoke gases, is not washed out again by the rain, and the recognition of smoke injury by this means is not possible.

"14. There is not known an absolutely certain botanical means of recognizing damage caused by sulphurous acid, but it is only possible to determine its presence through the combined evidence of the external and internal injuries. The surest proof is the chemical analysis for sulphuric acid."

Concerning paragraph 5 it should be noted that in the open country one seldom finds sulphur dioxide acting for a long continued time in one place. Ordinarily the smoke is blown about by the wind, thus making its action upon plants at a given place intermittent. During periods when the smoke is not present the plants show a tendency to recover.

The statements of paragraphs 3, 8, 9, 13 and 14 should be borne in mind when one compares the work of chemists who have experimented with pines, firs and other conifers, with that of chemists who have studied injuries caused by sulphur dioxide acting upon lucerne, sugar beets, beans, peas and other plants with soft succulent leaves.

Most of the experiments with plants thus far reported have been carried out with potted specimens or with such as grew in greenhouses. Of course under these more or less artificial conditions one might expect to obtain results somewhat different from those given

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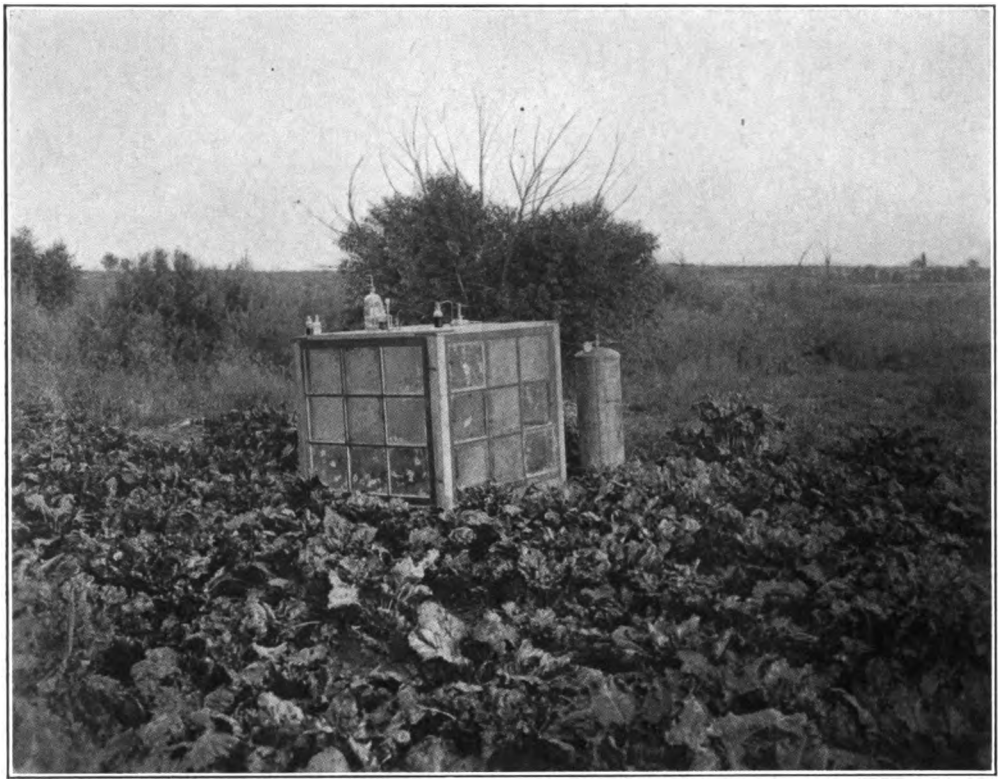


FIGURE 2.
Cabinet for Use in Fumigation Experiment.

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by field plants growing in place, consequently in all our experiments we used only field plants.

A sectional cabinet was built so as to be transported readily. (Fig. 2). Through the top were suspended several thermometers, a fan for causing a mixture of the gases, and an inlet tube for the sulphur dioxide. This inlet tube consisted of one leg of a tube provided with a two-way stop-cock, another branch of which led through a bottle containing a known amount of iodine solution. When ready for an experiment the plants surrounding those selected for the trial were cut away, and the ground was loosened up in order to let a square frame rest securely upon it. The cabinet was then placed upon the frame, the door shut, and earth piled about the base. The dimensions of the cabinet (four feet on a side) and the temperature and pressure of the atmosphere being known, it was possible to calculate how much sulphur dioxide, by volume, would be required to give in the cabinet a mixture of gases containing a known quantity of this active constituent. A definite amount of standard iodine solution, equivalent to a known volume of sulphur dioxide, was placed in the absorption bottle, a steady stream of sulphur dioxide admitted to it through one leg of the two-way tube, and the time required for decolorization of the iodine and starch carefully noted. At the end of the operation the stop-cock was quickly reversed and sulphur dioxide admitted to the cabinet long enough to give in it a mixture of the required concentration. As a check upon the accuracy of the first measurements and upon the steadiness of the gas current, a second known quantity of iodine was placed in the absorption bottle and the current of gas diverted to it at the conclusion of the "charging" of the cabinet, and the time required for decolorization again noted. The pressure of the gas in the tank being rather high and the amount of sulphur dioxide used in an experiment being rather small, it was believed that the current would be steady during the time of charging, that the measurements would be accurate to within at least ten per cent. and that the results would be preferable to those obtained when a sulphur-bearing compound was burned in a cabinet to generate a known amount of sulphur dioxide. With the aid of this cabinet, experiments were carried out upon sugar beets and alfalfa growing in a certain field about one and a half miles south of Bingham Junction, Utah. The dilute sulphur dioxide was allowed to remain in contact with the plants one hour and was then removed by opening the door and permitting fresh air to enter. After a known interval the process was repeated. Six or seven fumigations daily were carried out, the cabinet being allowed to remain open at least an hour between treatments and from 8.00 P. M. until 7.00 A. M. in cases where the experiment required more than six or seven fumigations.

In the case of lucerne (alfalfa) two treatments with sulphur dioxide

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equivalent to one part in ten thousand caused a slight wilting. Three more treatments caused incipient bleaching as well as withering. At the end of the seventh treatment the plants were quite bleached.

Four treatments with sulphur dioxide equivalent to one part of the gas in twenty thousand of air caused wilting, but no bleaching. Incipient bleaching was noted after the fifth treatment, and after the seventh fumigation the plants were decidedly bleached and withered.

Eight treatments with sulphur dioxide equivalent to one part of the gas to fifty thousand of air caused wilting, but practically no bleaching. After the ninth treatment bleaching was observed, and continued to become worse with succeeding fumigations. Even after twelve treatments the lucerne did not look so badly as did that which had been treated with a more concentrated sulphur dioxide only half that number of times. A series of experiments run as a "dummy" or blank, in which all the operations were carried out for a whole day just as in regular determinations, except that no sulphur dioxide was used, resulted in no evident injury to the plants treated.

In the case of sugar beets two treatments with one part of sulphur dioxide to ten thousand of air caused very evident wilting, accompanied by blackening. Bleaching began with the third treatment and increased to the fifth, when the plants were thoroughly ruined so far as their foliage was concerned.

Analogous results were obtained with sulphur dioxide one half as strong as the above, and the operation was discontinued after the seventh fumigation.

Twelve treatments with one part of sulphur dioxide to fifty thousand parts of air produced no visible injury. The same plants were then treated with one part of sulphur dioxide to thirty-three thousand parts of air, and after three more treatments slight wilting was evident. Fumigations were then stopped, but several days later these wilted spots, under the influence of the sunlight, presented a marked bleached effect.

Thus it will be seen that sulphur dioxide, when diluted to the amounts that can be present in the air of a smelting district, must be applied repeatedly to plants in order to cause material injury. Contrary to the statement of Haselhoff and Lindau (paragraph 9 above) observations of field conditions in this vicinity seem to show that damage is rare during bright, clear dry weather, but usually occurs during damp, "heavy" weather. With this fact in mind our fumigations were carried out in the presence of sufficient moisture to simulate these worst conditions, and we have every reason to believe that had less moisture been present in the cabinet the injury shown would have been less in amount. The temperature range during the experiments was normal for the time of year (August and September).

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A series of experiments with sulphur dioxide in aqueous solution, sprayed and poured upon alfalfa and sugar beets, was carried out. Solutions containing 2.91, 2.33, 1.75 and 1.46 grams of sulphur dioxide per liter when *sprayed* upon beet plants, using an atomizer, produced but slight effects, simply a few spots of yellow to white corrosion here and there. The same strengths of solutions when *poured* upon beets caused considerable corrosion. The latter statement applies also to solutions containing 1.17 to 0.87 grams of sulphur dioxide per liter when poured upon the beets. Weaker solutions than the above, whether sprayed or poured, produced little, if any injury. (See Table 2). In each experiment the leaves were treated with the reagent once only.

Analogous statements can be made concerning lucerne, but the action is far less marked.

As a corollary it might be said that solutions of sulphuric acid in quantities equivalent to the sulphur dioxide mentioned above, if present to the extent of 1.38 grams per liter or stronger, produced marked corrosion, whether sprayed or poured upon the plants. More dilute solutions (0.46 grams per liter or less) when used upon beets caused but little, if any, damage. (See Table 3.) Lucerne seems to possess slightly greater power of resistance to sulphuric acid than does the sugar beet.

For several reasons the question of the solubility of sulphur dioxide in water has a peculiar interest. By some the suggestion has been made that this gas be removed from the smoke by means of a suitable scrubber. By others it has been claimed that the fog and rain dissolve large quantities of sulphur dioxide and thus cause great damage to substances with which they come in contact. A few considerations concerning the possible strengths of solutions that could be formed from the gas in smelter smoke may not be out of place.

According to Schönfeld[1] pure sulphur dioxide, if allowed to remain in contact with water, will be dissolved or absorbed to the following extents at the temperatures stated:

Temperature.	Pressure.	Volume of Sulphur Dioxide per Volume of Water.
32° F	760 mm.	79.8
41	"	67.5
50	"	56.6
59	"	47.3
68	"	39.4
77	"	32.8
104	"	18.8

Applying the well known law of partial pressures of gases to such gas mixtures as escape from smelter stacks at this altitude, we find that the

[1] Ann., 95, 5.

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TABLE 2.

Experiments to Determine the Effect of Aqueous Solutions of Sulphur Dioxide upon Sugar Beets.

Plant Number.	Treatment.	Result on Leaf.	Beet Measurements. Length	Circumference.	Weight.	Polariscope.	Condition at time of analysis.
255	SO_2 2.91 g/l Sprayed	Corroded in a few small spots.	See Table No. 14.				
256	" " Poured	More corroded than 255.	9 in.	9 in.	13.5 oz.	15.2	Soft.
257	" 2.33 g/l S	Corroded in a few small spots.	See Table No. 14.				
258	" " P	Much corroded over large areas.	9	14	35.5	13.0	Hard.
259	" 1.75 S	Corroded in a few small spots.	8	10	13.5	15.6	Rotten half way up core.
260	" " P	More corroded than 255.	9	10.75	18.5	14	Soft.
261	" 1.46 g/l S	Corroded in a few small spots.	12	14	39	13.4	Hard.
262	" " P	More corroded than 255.	10	9	10.5	18.6	Rotten places at core.
263	" 1.17 S	Little injury, if any.	12	12	26.5	17.0	Soft.
264	" " P	More corroded than 255.	7	8	7	20.0	Soft.
265	" 0.87 S	Little injury, if any.	7.5	9.5	9.5	18.6	Soft.
266	" " P	More corroded than 255.	9	11	18	12.8	Soft.
267	" 0.58 S	Little injury, if any.	10.5	13.75	34	13.8	Hard.
268	" " P	" "	14	14.5	41	16.8	
269	" 0.29 S	" "	11	10.75	23.75	14.8	Hard.
270	" " P	Some white spots.	9	12	24.5	14.2	Hard.
271	" 0.15 S	Ditto No. 263	10.25	17	35.5	14	Hard.
272	" " P	" 263	11	14.5	42	15.8	Hard.
273	" 0.06 S	" 263	11	11.5	24.5	17.2	Hard.
274	" " P	" 263	13	11	26	16.4	Hard.
275	" 0.03 S	" 263	7.5	9	9.5	18.0	Hard.
276	" " P	" 262	10.5	13	28	15.8	Soft.

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following volumes of sulphur dioxide could be absorbed by one volume of water:

Average Sulphur Dioxide by Volume,		Min. 0.75%	Max. 3.00%
Temperature.	Pressure.	Volume of Sulphur Dioxide per Volume of Water.	
32° F	650 mm.	0.56	2.04
41	"	0.43	1.70
50	"	0.36	1.42
59	"	0.30	1.20
68	"	0.25	1.00
77	"	0.21	0.83
104	"	0.12	0.48

Attempts to prepare a saturated solution of sulphur dioxide from the flue gases of a certain smelter in August, 1906, resulted in solutions that contained as a maximum 0.33 volumes of sulphur dioxide per volume of water. As the temperature at the time of the experiment varied from 95 to 102° F. and the sulphur dioxide content of the gas from 1.3 to 1.5 per cent., the concordance of the theoretical and the actual values is sufficiently close for all practical purposes. To an atmosphere containing less than the indicated percentages of sulphur dioxide, under the given conditions of temperature and pressure, the said solutions would give up some of their sulphur dioxide and thus become weaker. These conditions would obtain as soon as the gases had escaped from the stack and had a chance to diffuse.

The possibility of dissolving sulphur dioxide from the smoke and thus eliminating the "smoke nuisance" is thus seen to be very slight indeed, especially in a semi-arid district where water is valuable. And granting that the gas could be so dissolved, what disposition could be made of the product?

Directing attention to the injury caused to plants by "flue dust" we must state at the outset that by this term we mean *not* the gross heavy material that settles in the flues near the furnaces, roasters or reverberatories, but the finely divided substance that finds its way to the stack and even out of the stack. The term "solid emanation" would probably be a better name than "flue dust." It was noticed some time ago that a cold body, such as a tube cooled by a current of air, held into a stack condensed upon its surface a deposit of solid matter. This solid matter resembles that which is found at the terminus of a long flue system or at the top of a stack. The analogy in composition is shown by Table 4. Dust No. 3 consisted of a concretion and mass of dust broken from the top of a stack; Dust No. 4 was taken from flues near the roasters, and Dust No. 8 from a flue leading from copper blast furnaces, but not at the base of the stack. The results obtained from these three samples are scarcely comparable with those obtained from the six others,

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which were either collected at the end of a long flue system or by condensation upon tubes, as referred to above.

TABLE 3.

Experiments to Determine the Effect of Dilute Solutions of Sulphuric Acid upon Sugar Beets.

Plant Number	Treatment.		Result on Leaf.	Length	Circumference.	Weight.	Polariscope	Condition at time analysis
277	H_2SO_4 .6g/l	Sprayed.	Badly corroded, small white and brown spots.	13	18.25	73 oz.	13.2	Hard
78	"	Poured.	Badly corroded, over large areas.	12	14.5	38	13.2	Soft
79	" 2.76	S	Ditto No. 277	See Table No. 14.				
80	"	P	" 278	13.5	9.5	23	17.8	Soft
81	" 1.38	S	" 277	10	12.5	33	16.8	Soft
82	"	P	" 277	10.5	10	16	20.2	Soft
83	" 0.46	S	Little injury, if any	9.5	12.25	24	18.0	Soft
84	" "	P	" "	14	13	40	13.6	
85	" 0.23	S	" "	10	12	28	14.6	Hard
86	" 0.23	P	" "	13	14	36	16.8	Hard
87	" 0.09	S	" "	11.5	15	45.5	15.4	Hard
88	" "	P	" "	9	13.5	32	18.8	Hard
89	" 0.05	S	" "	11	11	32.5	16.0	Soft
90	" "	P	" "	9	12	27	18.4	Hard

TABLE NO. 4

Analyses of Flue Dust

	Moisture Per cent.	Water Sol. "SO_3" Per cent.	Total "SO_3" Per cent.	Water Sol. Fe Per cent.	Total Fe Per cent.	Water Sol. Cu Per cent.	Total Cu Per cent.	(SiO_2) Insol. Per cent.	Pb Per cent.	As. Per cent.	Zinc Per cent.
Flue Dust 1....	2.0	15.7	26.8	3.3	15.2	1.6	5.1	21.6	6.0	9.75	0.65
" " 2....	0.7	14.2	27.3	3.6	18.3	0.5	3.5	22.9	10.7	6.14	.95
" " 3....	4.1	17.7	33.9	3.6	16.7	1.6	4.2	28.5	0.8	.83	.15
" " 4....	0.1	6.7	20.6	0.2	8.1	Trace	2.2	31.4	16.3	1.31	4.40
" " 5....	0.3	6.1	21.0	0.8	10.3	Free	1.0	18.0	19.7	13.52	4.25
" " 6....	0.9	6.9	24.4	0.7	9.4	"	0.3	16.6	24.1	10.26	1 25
" " 7....	3.3	17.8	29.0	4.2	9.6	0.8	1.5	15.8	15.5	6.00	1.90
" " 8....	0.7	2.3	31.8	0.0	33.0	Free	3.7	27.4	2.4	.47	.95
" " 9....	not analyzed.										

It has been suggested that the corrosive power of the dust is due to the presence of sulphur trioxide closely associated with the solid particles, but not necessarily in combination with them. In the roasting process conditions are especially favorable for the production of sulphates, which afterward break up into metallic oxides and sulphur trioxide. Moreover the metallic oxides formed from the burning of sulphides are recognized as good catalyzers, and in their presence it is not improbable that some of the sulphur dioxide at first produced may unite with the excess of oxygen necessarily present. To test the hygroscopic power—which may be accepted as an indication of the sulphur trioxide content—of the dusts used in these tests, weighed samples were placed on watch

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glasses and supported over water, but protected from the outer air by improvised bell jars. At intervals the powders were weighed, and after the lapse of two hundred hours were dried to constant weight at 105°. The following table gives the per cent. of moisture originally present and the moisture content after twelve, twenty-four and forty-eight hours:

TABLE NO. 5.

	Moisture Content Originally. Per cent.	Moisture Content after Twelve Hours. Per cent.	Moisture Content after Twenty-four hours. Per cent.	Moisture Content after Forty-eight hours. Per cent.
Dust No. 1	2.04	16.22	21.83	23.36
" 2	1.76	10.17	14.40	16.59
" 3	4.23	10.21	12.05	13.09
" 4	0.09	3.39	5.20	5.60
" 5	0.35	3.01	5.87	6.87
" 6	0.91	2.98	4.19	4.44
" 7	3.43	5.80	9.88	11.48
" 8	0.69	1.56	2.78	1.67

With the exceptions of Dusts No. 5 and No. 6 it was found that the corrosive power was roughly proportional to the hygroscopic power, but that in these two instances, although the corrosive power was great, the hygroscopicity was low. Could their corrosiveness be due to their high arsenic content?

Unlike stack gases, which are diluted and carried great distances,—upward, as well as in other directions—by the process of diffusion, solid emanations are bound to settle. For them there is no fortunate diffusive action. By the use of dust collectors one can gather samples of this material even at considerable distances from a smelter. Near a smelter unprovided with good dust- or fume-arresting devices one can even find particles of appreciable size settling upon the clothing, and if these little particles be touched with the tongue their acrid, burning property is made manifest. The analyses of hay gathered from stacks and sheds (Table 6), dust collected from rafters in protected places (Table 7), soil from particular localities (Table 8), and the viscera of animals said

TABLE NO. 6.

Partial Analyses of Lucerne Collected in the Smelter Zone.

		Pb.	Cu Per cent.	As. Per cent.
Sample No. 4	Lucerne	Absent	0.0024	Trace
" 11	"	Absent	.0012	Trace
" 17	"	Trace	Trace	0.001
" 19	"	Trace	0.002	0.001
" 30	"	Trace	0.006	Trace
" 31	"	Absent	0.006	Absent

to have been poisoned by pasturing in parts of the "smoke zone," show that some of the solids thrown out from the stacks find their way considerable distances, the maximum amount, of course, being distributed in the directions of the prevailing winds. The quantity of solids thrown out by a given smelter naturally depends upon the nature of the ore used, the metallurgical processes employed, the extent and kind of fume-

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arresting devices installed, and possibly upon other factors.

TABLE NO. 7.

Partial Analyses of Dust Gathered from Rafters in Barns, Sheds, etc.

		Pb. Per cent.	Cu. Per cent.	As. Per cent.
Sample No. 5	Dust from Rafters in Shed	Trace	0.912	Trace
" 8	" " "	Absent	0.057	Trace
" 9	" " "	Trace	0.337	Trace
" 10	" " "	Trace	0.255	Trace
" 16	" Gutter around house	0.185	0.160	0.051
" 23	Dust from Rafters in Shed	0.069	0.024	0.003
" 24	" " "	Trace	0.088	0.009
" 27	" " "	0.338	0.235	0.121
" 29	" " "	Trace	0.036	0.006
" 32	" " "	0.124	0.167	0.049

[1] Lead and arsenic not determined quantitatively.

TABLE NO. 8.

Partial Analysis of Soils.

		Pb. Per cent.	Cu. Per cent.	As. Per cent.
Sample No. 22	Soil	Trace	0.018%	0.004%
" " 21	"	Absent	Absent	Trace

Several series of experiments with "dust" upon sugar beets and alfalfa were carried out. In Series No. 1 the dust was treated with water, solutions representing 3, 2, 1 and 0.5 per cent. of the solid being made. These solutions were sprayed upon plants and the result in general was very severe corrosion. One treatment was given to each plant. As was to be expected Dusts No. 4 and No. 8 were scarcely injurious at all, and Dust No. 3 occupied an intermediate position in this respect between the coarse materials (No. 4 and No. 8) on the one side and the fine dust (No.'s 1, 2, 5, 6, 7 and 9) on the other. (Table 9).

In Series No. 2 Dust No. 2 was mixed with soil in varying quantities at dusted upon the plants. A mixture of the dust with nine times its weight of soil produced practically no effect upon the plant, but in cases where the dust made up twenty per cent. or more of the mixture the results upon the plants were literally "frightful." It would seem that the corrosive power of the solid emanation is neutralized in whole or in part by mixing it with a sufficient quantity of soil. (Table 10).

TABLE 10.

Experiments to Determine the Effect of Mixtures of Flue Dust and Soil upon Sugar Beets.

Plant Number.		Treatment.	Result on Leaf.	Length.	Circumference.	Weight	Polariscope.	Condition at time of analysis.
213	100%	Flue Dust No. 2	Ditto 201. All leaves	11	16	58	14.8	Soft
214	50	" "	frightfully corroded	9.5	13.75	27.5	19.6	Hard
215	20	" "	" "	10.5	13.0	23.5	17.0	
216	10	" "	Corroded but little	10	11.75	21.75	19.0	
217	5	" "	Little injury, if any	See Table No. 14.				
218	3	" "	" "	7	10	13.5	18.8	Hard
219	2	" "	" "	7.5	10.5	14.25	16.4	Hard
220	1	" "	" "	See Table No. 14.				
221	0.5	" "	" "	7	9.25	9.5	21.8	

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TABLE 9.

EXPERIMENTS TO DETERMINE THE EFFECT OF AQUEOUS SOLUTIONS OF FLUE-DUST UPON SUGAR BEETS.

Plant number	Treatment		Result on Leaf	Length	Circumference	Weight oz.	Polariscope	Condition at time of Analysis
201	3%	Solution	Very badly corroded	13in	14 in.	41.5	12.4	Hard
202	2	Flue	" " "	13.5	13	32	12.4	Hard
203	1	Dust	" " "	12	13	31.5	17.4	Soft
204	0.5	No. 1	" " " not so extensive	12	16	45	13.4	Hard
205	3%	Solution	" " "	12	12	22.5	13.8	Hard
206	2	Flue	" " "	8	9.5	13.0	14.8	Hard
207	1	Dust	" " "	11	16	43	15.6	Hard
208	0.5	No. 9	" " "	12.5	13.5	38	18.8	Hard
209	3%	Solution	Ditto No. 201	11.0	14.5	36	12.6	Hard
210	2	Flue	Ditto No. 204	14.0	15.0	44	17.6	Hard
211	1	Dust	"	9	10.25	15	19.6	
212	0.5	No. 2	"	10.5	13	34.5	13.6	Soft
222	3%	Solution	Corroded in spots	13	14.0	45.0	15.6	
223	2	Flue	" but not so marked. See table No. 14					
224	1	Dust	" " " " "					
225	0.5	No.3	"	11	17	52.5	13.2	Hard
226	3%	Solution	Corroded in spots	14	14.75	50	17.0	Hard
227	2	Flue	Little corroded	18	13	41.0	15.4	
228	1	Dust	" "	14	13.5	36.75	14.4	
229	0.5	No. 4	" "	13.5	13	32.5	16.2	Hard

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TABLE 9 (Continued.)

Plant number	Treatment	Result on Leaf	Length in.	Circumference in.	Weight oz.	Polariscope	Condition at time of analysis
230	3% Solution	Very badly corroded. See Table 14.					
231	2 Flue	" " "	10	10.5	18	14.2	Hard
232	1 Dust	" " " , but not so extensive	14	13.5	42.5	16	Hard
233	0.5 No. 5	Little corrosion evident	13	14.5	41.5	13.6	Hard
234	3% Solution	Very badly corroded	14.5	14.5	34.0	15.2	Hard
235	2 Flue	" " "	14	11.5	22.5	17.4	
236	1 Dust	" " "	10.5	13.5	38.5	17	Soft
237	0.5 No. 6	" " "	8	13.75	31.5	16.8	Hard
238	3% Solution	" " "	9	16.75	51	16	Hard
239	2 Flue	" " "	13	12	30.5	15.8	Hard
240	1 Dust	" " "	10	13	37	16.8	Soft
241	0.5 No. 7	" " " but not so extensive	9.5	14	36.5	13.8	Hard
242	3% Solution	Little damage if any	11	13.75	41.5	15.8	Hard
243	2 Flue	" " " "	10	17	41.5	14	Hard
244	1 Dust	" " " "	10	10	17	21.4	Soft
245	0.5 No. 8	" " " "	9.5	14.5	38.5	16.8	Hard

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In Series No. 3 each sample of dust was mixed with twenty-five or thirty times its weight of water and the plants were sprinkled with the mixture. (Table 11.)

TABLE 11.

Experiments to Determine the Effect of Mixtures of Flue Dust and Water upon Sugar Beets.

Plant Number.	Treatment.	Result on Leaf.	Length.	Circumference.	Weight.	Polariscope.	Condition at time of Analysis.
246	Flue Dust No. 1	Very badly corroded.	14	13.5	42.5	11.0	Hard
247	" " 9	" "	10	10.75	21.0	15.6	Soft
248	" " 2	" "	11	12.75	25	17.2	Hard
249	" " 3	" " but not so extensive	11.5	14.5	41.5	14.0	Hard
250	" " 4	Very badly corroded	10.5	15.0	44.0	15.8	Hard
251	" " 5	Slight injury in a few places	13.0	12.75	31.0	14.8	Hard
252	" " 6	Very badly corroded	9	15.25	39	8.2	Rotten at point
253	" " 7	" "	8	12	27	13.4	Hard
254	" " 8	Uninjured	8	10.5	18	17.8	Hard

One is impressed with the facts that the finely divided "dust" or fume from either a lead or a copper smelter is extremely corrosive in its action upon vegetation, that the gross particles of dust that settle out in flues or chambers near the roasters, blast furnaces, reverberatories etc. are almost without effect upon plants, and that the corrosive power of even the worst materials is neutralized in whole or in part by mixing them with soil. The latter fact fortunately precludes the possibility of the dusts exerting a cumulative action, which would increase the amount of damage from year to year.

Although these plants were treated in August, after they had attained considerable growth, it was deemed wise to collect the beets at the time of the regular harvest in October, measure their length and circumference, obtain their weight and determine their sugar content. For the latter purpose the beet pulp was extracted with water at a temperature of 80° for thirty minutes, clarified with lead acetate and sodium sulphate solutions, cooled to 17.5°, filtered and polarized at that temperature in a Schmidt and Haensch triple field instrument employing a 200 mm. tube. To obtain the percentage of sugar used as a basis of settlement by the Utah Sugar Company at the time these analyses were made, multiply the doubled polariscope readings given in the various tables by the factor 0.90. In Table 12 are given the measurements of some uninjured, untreated beets grown in the field where the main experiments were carried out. In Table 13 we have the results obtained with certain beets grown in a field exposed to the smelter smoke. In this field the visible injury seemed to reach a maximum. Table 14 is

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given merely for the sake of completeness. It shows the measurements made upon beets whose labels had become somewhat blurred during transit. Table 15 gives a summary of the results upon the beets. All the beets studied were classified as either "injured" or "uninjured", and then the beets of approximately the same weight in the two classes were compared with each other. The results bear out the oft-quoted statement that small beets are richer in sugar than the large ones, and show that the average difference in the sugar content of the "Injured" and "Uninjured" beets is comparatively small. It proves that the yield in tons per acre is a better criterion of damage than the percentage sugar content of the beets.

TABLE 12.

Uninjured Beets Selected for Comparison Purposes.

		L.	Circ.	Weight.	Polar.	
1	Uninjured	10	12.	20.5	17.6	Hard
2	"	13	15.5	46	14.6	Hard
3	"	15	13.25	41	14.8	
4	"	10	13.5	29	18.6	Hard
5	"	12.5	12.5	37	15.6	Hard
6	"	12.5	14.25	38	14	Hard

TABLE 13.

Beets from a Badly Damaged Field, Selected for Comparison Purposes.

		Length.	Circumference.	Weight.	Polariscope.	Condition at time of Analysis.
A	Leaves badly affected	9.5	8.0	10.25	16.4	Soft
B	" "	10	9.5	12.5	17.2	Shrunken
C	" "	7.5	7	6.5	19.0	Soft, shrunken
D	" "	10.5	11.0	17.5	16.6	Hard
E	" "	9.75	9.0	27.75	11.4	Soft, shrunken
F	Uninjured	13	16	61.5	13.2	Hard
G	"	10	11.5	25.0	17.2	Soft, shrunken
H	"	6	7.25	5.5	19.0	Soft
I	"	10	10.5	14.5	16.4	Soft
J	"	7	10.5	14.5	17.0	Hard
K	"	10	12	21.5	16.4	Hard
L	"	9.5	11.0	17.5	17.0	Hard

TABLE 14.

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Plant Number.	Length.	Circumference.	Weight.	Polariscope
23 (3) ?	9 in.	11.25 in.	20.5	18
21 ?	12	13.50	29.5	18
2 ? ?	14	13	38.5	15
? ? 4	14	14.5	48	12.8
2 ? ?	15	13.5	38	14.6
25 ?	8	13.75	34	11.0
?	12	17.0	58	11.0
? 9	15	14.5	42.5	15.4

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TABLE 15.

Summary of Beet Analyses.

Weight.	Uninjured plants. Number of Plants.	Uninjured plants. Average Polariscope.	Injured plants. Number of Plants.	Injured plants. Average Polariscope.
Less than 15 oz.	13	17.93	5	17.40
15–20	4	16.38	3	17.0
20–25	7	16.74	7	16.51
25–30	7	16.86	3	14.80
30–35	3	16.30	7	15.14
35–40	8	15.15	8	14.70
40–45	8	15.25	7	14.46
45–50	2	15.00	2	16.30
50–55			2	14.60
55–60			1	14.80
60 and over	1	13.2	1	13.20
Average,	53	16.39	46	15.64

Difference in favor of "Uninjured" Beets—0.75%.

In the case of lucerne it has been shown that material that had suffered greatly from the smoke possessed considerable value as forage. An extended series of feeding experiments conducted by L. A. Merrill, late of the Agricultural College of Utah, has proved this.[1] It is evident that a loss in value of a smoke-blighted crop is not necessarily proportional to its loss in beauty.

The appearances of leaves of lucerne and sugar beets grown in the smelter district show that much of the visible injury is entirely analogous to that produced when solid particles of "flue dust" are allowed to fall upon plants. One cannot deny, however, that some of the effects observed when a whole field is blighted within a short time in heavy, moist weather, resemble those produced by sulphur dioxide. By no means is sulphur dioxide to be considered as harmless, especially in an enclosed space and in a moist climate, but we are forced by the weight of the evidence to the conclusion stated in our introduction, *viz.*, that heretofore undue emphasis has been laid upon the injurious effects of sulphur dioxide upon growing plants, and that the harmful action of the solid emanations from the smelters—the so-called "flue dust"—has been seriously underestimated.

In conclusion the author must acknowledge his indebtedness to Messrs. Rawlins, King and Street, attorneys in Salt Lake City, for permission to use much of the matter embodied in this paper; to the Citizens Committee representing the farmers in the recent injunction suit; and to the managers of the Bingham Consolidated Mining and Smelting Company, through whose assistance the work was, in part, made possible. To Mr. W. S. Thomas, consulting chemist of the said company, are due

[1] Western Chemist and Metallurgist, 3, 59 (1907).

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the author's sincerest thanks for many suggestions and comments, both as to matter and methods, especially in respect to the problem of injury caused by the solid emanations.

UNIVERSITY OF UTAH,
January, 1907.

PAPERS ON SMELTER SMOKE.

(FIRST PAPER)

The Determination of Arsenic and Other Solid Constituents of Smelter Smoke, with a Study of the Effects of High Stacks and Large Condensing Flues.

BY W. D. HARKINS AND R. E. SWAIN.

Received May 2, 1907.

The determination of the constituents of smelter smoke is important for two reasons: many of the constituents have considerable commercial value, while a large number are poisonous in varying degrees to plant and animal life. Under the first class will come sulphur dioxide, sulphuric acid, copper, lead, zinc, arsenic, antimony, and certain other substances. It will be seen that these same substances belong in some degree to ehe second class as well, so that the solution of the problem of recovering the economic values from the smoke will also solve the problem of lessening or preventing its injurious action.

It will be the purpose of a series of articles, of which this is the first, to point out the chemical facts which make the solution of these problems so essential to the welfare of many extensive districts in the west, as well as to some in the east and south of our country. The work which led to the publication of this special article, was the estimation of the amount of arsenic expelled from the greatest of the world's smelters—a plant which has a capacity of ten thousand tons of ore per day, and the output of which for 1906 was estimated as eleven and one half per cent. of the world's production of copper. Compare with this the Freiburg smelters at the time of the work of Haubner[1], Sussdorf[2], Freytag[3], taking the date 1870. At this time the two smelters, the Mülden and Halsbräcken, treated daily about seventy tons of ore. According to Haselhoff and Lindau[4], all the smelters of the Lower Hartz use annually only sixty-three thousand tons, this being the amount for the year 1899. In this country, the Garfield Beach smelter, Utah, is to be enlarged to a capacity of eight thousand tons per day, while the Great Falls, Montana, smelter has now a capacity of three thousand five hundred tons

[1] Haubner, Die durch Hüttenrauch veranlassten Krankheiten des Rindviehes im Hüttenrauchsbezirke der Freiberger Hütten (Arch. f. wiss. u. prakt. Tierheilk. 1878, 4, 97-136; 241-260.)

[2] Sussdorf, Allg. Deut. Naturhist. Ztg., Hamburg, I (1855), No. 3, 97.

[3] Freytag, M., Jahrb. f. d. Berg-u. Hüttenwesen im Königr, Sachsen auf das Jahr. 1873, Abh. 3. ——, (l. c. 1875, Abh. 3).

[4] Haselhoff und Lindau, Rauch-Beschädigung, p. 147.

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per day, and will soon be made much larger. In Nevada, the Ely smelter is to treat from ten to twenty thousand tons of ore per day. Many other great plants could be named, but these examples are sufficient to show that the problem of injury by smoke is a much more important one in this country than it is in Germany, at least in so far as the magnitude of the smelting operations themselves is concerned.

During the last few years there have been numerous complaints from smelter districts, that the trees and grass are not only injured in their growth by the sulphur dioxide and sulphuric acid of the smoke, but in some way the grass is also rendered poisonous for horses and stock, probably as the result of the deposition of mineral poisons. This calls to mind the investigations made in Germany in the year 1849 by Stockhardt,[1] and in 1853 by Stockhardt aud Frange,[1] who decided that the poisoning caused by smelter smoke was due to the action of lead. However, the later investigations of Sussdorff and Haubner, as referred to above, show conclusively that the principal damage was caused by arsenic, and not by lead.

The investigations which led to the publication of this series of articles on smelter smoke, were begun by one of us (Harkins) in the year 1902, about ten months after the completion of the smelter. The smoke and the grasses of the district were found to contain considerable arsenic, while small quantities of this element were found in the organs of herbivorous animals living in the vicinity of the smelter. For many years previous the ore had been treated in a plant which cost in all about six million dollars, but in January 1902 this was abandoned for the present smelter, in order to reduce the cost of smelting by the adoption of improved methods. The stone and brick settling flues, which in the old works served to carry the smoke to the tops of the hills upon which the stacks were built, were in the new works replaced by large condensing chambers of brick. These chambers averaged about forty feet wide, forty feet high, and two hundred and sixty feet long; but the volume utilized in settling the flue dust was somewhat less than this, since ten feet of the height was taken up at the bottom by a passageway for the cars that carry the dust to the reverberatory furnaces. The volume of each chamber was therefore about three hundred thousand cubic feet. One was attached to the roaster building, one to the blast, and one to the converters, and each was provided with a separate steel stack, twenty-two feet in internal diameter, and two hundred twenty-five feet high. The smoke from the reverberatory furnaces was discharged directly into a stack of the same dimensions.

Whether or not the settling chambers were less effective than the long flues of the old works, is very difficult to say; but it certainly is

[1] Opinion transmitted to the Royal Minister of the Interior, 1854.

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a fact, that during the year after the erection of the new works the loss of animals in the valley became very much greater than before. This was due in part to a difference in the location of the smelters, since the new smelter was built closer to the valley lands, and in such a position that the prevailing winds carried more of the smoke across the farms of the district. Even if it is possible that some of the increased poisonous action of the fields upon the animals was due to a difference in the composition of the smoke, owing to a change in the methods of smelting, still it is certain that much valuable material, somewhat poisonous, was thrown out by the old works. The ground surrounding them became so rich in copper that a very large amount of this metal was obtained by smelting the top soil of a considerable area.

As a result of the operation of the new smelter, the losses of stock in the valley during the year 1902 were so heavy, and the hay and grass, on analysis, showed so much arsenic, that a great system of flues was built in order to settle the copper, and to condense the arsenic trioxide. The latter escaped in large quantities as a gas, especially from the blast and McDougall roasting furnaces. The system of flues built at this time, is the largest in the world, and a study of its effects in settling different compounds presents many interesting chemical problems, only a few of which can be touched upon here.

This first set of flues joins all the furnaces to one great flue, the smoke from three of the buildings passing through the settling chambers before entering the flues at all. Of the connecting flues the blast furnace flue is 1653 feet in length; the reverberatory flue, 842 feet; the roaster flue, 488 feet; and all are twenty feet wide and twenty feet high. The converter flue is at present 703 feet long, 18 feet wide, and 10 feet high. All these join in one great flue, and for twelve hundred feet this is sixty feet in width, with twenty foot side walls. The bottom slopes down on both sides to hoppers in the middle, which open into cars underneath. It is 36 feet from the top of the flue to the bottom of the excavation, and the area of the cross section of this portion is 1600 square feet. Above this there are two parallel sections, each 1000 feet long, and of the same dimensions as the single flue, making a double flue, 120 feet wide, with a cross section of 3200 square feet.

The volume of the original settling chambers is about 900,000 cubic feet, while that added in 1903, in the form of new flues, is about 6,000,000 cubic feet, making the volume available for settling the solids of the smoke practically seven and one half times as great as before. In order to cool the gases, the 120 foot flue is covered with a roof made of thin pieces of sheet steel, supported by I beams underneath. This flue lies on a steep mountain side, and ends at the top in a big stack, 31.33 feet in internal diameter, 44.5 feet external diameter at the bottom, 30 feet internal

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diameter at the top, and three hundred feet high. The smoke is admitted to the stack by two openings on opposite sides, each 12.5 feet wide by 34.5 feet high. The elevation of the top of the stack is 6,186 feet, and of the reverberatory furnaces, 5442 feet, or a difference of seven hundred feet. The top of the stack is eleven hundred feet above the valley below.

The great flues and stack were built in order to settle the arsenic and copper, and to prevent the damage to the forests and crops from the sulphur dioxide of the smoke. After a year and a half of operation, it was claimed by the smelter company that these results were accomplished, and that practically all of the arsenic was deposited in the flue and chambers, while the stack raised the smoke to such a height that the sulphur dioxide did little damage to vegetation. The farmers of the district asserted on the other hand, that their animals were poisoned, and their crops damaged in the same way as before, though the distribution of the damage was somewhat different.

The velocity determinations and analyses of smoke which follow, and the more recent of the investigations in regard to the crops and animals, as given in the later papers, were undertaken to determine the real efficiency of this flue and stack.

The Determination of Velocity.—In sampling and analyzing smoke, among the most difficult problems is one which may seem to belong to the engineer, but which, our experience has shown, cannot be left to the ordinary man in this profession. Since the results of his analyses depend entirely for their calculation upon the volume of the smoke given off, it becomes the duty of the chemist to make these volume or velocity measurements

In the determination of the velocity of moving gases there are only two methods which have any claim to accuracy. These are the determination by the Pitot tube, and that by the ordinary wheel anemometer. A method much used by smelter men consists in releasing a piece of charred paper, and noting the time which it takes to rise to the top of the stack. This is manifestly a very crude method, and is not applicable in the case of very large stacks, since it is impossible to see the charred paper when it first leaves the top of the stack. Another method sometimes used is to obtain the difference in pressure between the outside and the inside of the chimney.

The Pitot tube was devised by Pitot[1] in 1732, and was used for the determination of the velocity of water. It consisted of an L tube with the ends of the two arms open, but with the horizontal arm drawn down to a small opening. When turned with the horizontal arm pointing up stream, the impact of the stream on its mouth balanced a column of

[1] Pitot, Histoire de l'Académie des Sciences (1732), p. 376.

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water in the vertical arm of a height equal to the square of the velocity divided by twice the coefficient of gravity. When the plane of the mouth of the tube was placed parallel to the motion of the stream, the level of the water inside and outside the stream was practically the same. When two tubes are placed thus at right angles with each other and connected with a differential manometer in which the liquid is the same as the moving liquid, the difference of level in the two arms of the manometer is the same as that given above, or $h = \frac{v^2}{2g}$. An instrument of this kind was devised by Darcy, and is known as a Darcy gauge, or a modified Pitot tube.

The principal of the Pitot tube was developed from the proposition of Toricelli[1] by Daniel Bernoulli[2], who used as a basis of his development the principle of the *conservatio virium vivarum.* He proved that in a steady stream of a frictionless liquid, loss of energy of motion is accompanied by an equivalent gain of head, and gain of motion energy by an equivalent loss of head. The head may be in the form of elevation of the liquid or of pressure, or of both combined. In other words, when kinetic energy is converted into potential, or potential into kinetic, the loss of kinetic energy is accompanied by an equal gain in potential energy, and the gain of kinetic energy by an equal loss of potential energy. Expressed in symbols:

$$mgh = \tfrac{1}{2}\, mv^2$$

or

$$v = \sqrt{2gh}$$

This is the last formula of the Pitot tube, and is the same as the well known formula for the efflux of liquids.

Although there has been considerable dispute as to the practical formula of the Pitot tube, the experiments of Darcy, and also of most of the modern writers, show that in the formula $v = c\sqrt{2gh}$ the factor c is unity within the limits of experimental error, where the tube is of the proper construction. This is the view expressed by Freeman[3], White,[4] Williams,[5] Robinson,[6] and Gregory,[7] in recent articles upon this subject. The Pitot tube, when properly constructed, has proved an accurate instrument for the measurement of the velocity of either gases or liquids when the velocities are not too low. Nearly all the early applications of

[1] Toricelli, De Motu gravium Projectorum (1643).

[2] Bernoulli, Hydronamica (1738).

[3] Freeman, J. R., Trans. Am. Soc. Civil Engineers, 21 (1889).

[4] White, W. M., J. of Assoc. Eng. Soc., 25 (1900), p. 161, and 27, (1901), pp. 35-67.

[5] Williams, G. S., Pr. Am. Soc. Civil Eng., May, 1901.

[6] Robinson, S. W., Trans. Am. Soc. Mech. Eng., 25 p. 208-211 (1903).

[7] Gregory, W. B., Trans. Am. Soc. Mech. Eng., 25 (1903).

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this apparatus were made in the determination of the velocity of liquids, usually the velocity of streams or of ships[1].

The tubes used for our work, as shown in Figure 1, consists of two

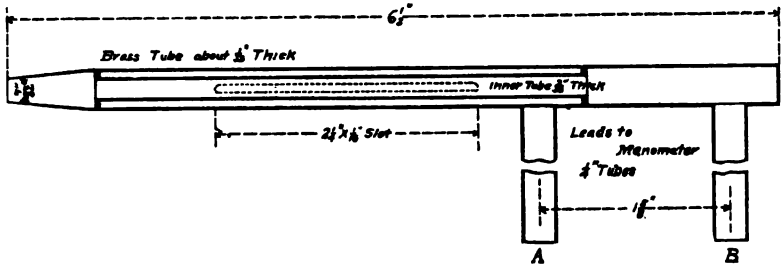


FIG. 1. Pitot tube as modified by Captain D. W. Taylor.

These tubes were made from a design furnished by Captain D. W. Taylor,[2] Naval Constructor at Washington. Tubes of this design had been used by him to test the ventilating fans of the battleship Missouri, and were previously tested by Prof. A. F. Zahm, of the Catholic University, Washington. Using the formula $v = \sqrt{2gh}$, the latter found that the results agreed with very accurate independent measurements of the volume of the air.

concentric tubes, each connected to one arm of a differential manometer, so that the latter gives the difference of pressure of the gas in the two tubes. The axis of the tube is placed parallel to the direction of motion of the smoke, and the inner tube has an opening 0.553 centimeters in diameter with its plane at right angles to the axis. The outer tube has a slot 5.71 centimeters long by 0.16 centimeters wide on each side, so that it gives to the manometer the static pressure of the gas. The inner tube corresponds to the original Pitot tube, and gives the static pressure plus the pressure caused by the impact of the gas upon its mouth, or what is often called the velocity pressure. The use of slots instead of the circular openings usually employed to obtain the static pressure, prevents the aspirating effects noticed in the ordinary form of the tube. The two tubes (A) and (B), each 0.63 centimeters in diameter, are provided with screw threads at the ends, and on these tubes iron pipes of the same diameter are fastened. In the velocity determinations these pipes varied in length up to twenty-three feet, and served to support the Pitot tubes in the stack and to connect it with the manometer. To make the support rigid they were stiffened by a band of steel, 1.3 centimeters thick and 4 centimeters wide, which fitted exactly between the two pipes (A) and (B). The pipes and the steel band were bound at distances of 60 centimeters by clamps of heavy steel, bolted together by 1.3 centimeter

[1] Berthon, E., The Engineer (1850); Pendred, Vaughn, The Engineer, Dec. 17, 1869; Rankine, W. J. M., The Engineer, Jan. 1870.

[2] Taylor, D. W., Eng. News, 52, 18, p. 387-89, Nov. 3, 1904.

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bolts. It was essential that these supports should be rigid, since the portions inside the wall of the stack had to be entirely self-supporting.

The manometer[1] used for this work was the simplest form possible and proved perfectly satisfactory. It consists of a glass U tube of a small even bore, laid upon the slant of a triangle having a base of 23.74 centimeters, a vertical side of 2.5 centimeters, and a slanting side of 25 centimeters. This was built of well seasoned wood, very carefully cut, and was fastened upon a broad horizontal base into which two levels were set. The U tube was bound down by copper wires, and a steel scale, accurate at 15°, was placed between the two arms. The two sides should be connected at the bottom by a horizontal spiral of the same glass tube, in order to lengthen the natural period of vibration of the ether column. The liquid used was ether, which responds freely to any change of pressure. It had a specific gravity of 0.7300 at a temperature of 17°. The manometer was connected to the Pitot tube pipes through two two-way cocks; and on reversing both of these, the impact arm of the manometer became the static pressure arm, so that the effect of any slight difference of level between the two side tubes was eliminated. Great care was taken to set the instrument in such a way that the two ends of the base of the triangle should be at the same level. For each reading the stopcocks were reversed several times, the average taken, and reduced to velocity by the formula, $V = \sqrt{\frac{2ghD_{ether}}{120\ D_{gas}}}$, where h is the reading expressed in inches.

Comparison of a Pitot Tube with an Anemometer.[2]—In order to see how the results obtained by the Pitot tube would compare with those given by a wheel anemometer, the two instruments were placed side by side, as shown in Figure 2. The pipe (A), running just beneath the concrete floor, connects a large fan, placed some distance from the section shown in the cut, with one of the main flues of the building where the tests were made. The Pitot tube (P) and the anemometer (M) were supported by the two 0.64 centimeter iron pipes (C), which connect with the two arms of the Pitot tube—the static pressure arm (S), and the impact arm (I). The tubes (C) were connected by the rubber tubes (R) to the differential ether manometer. The anemometer was stopped or started by the lever (L″), which was turned by means of a series of levers and rods (L,D,L′ and D′), arranged so that the recording mech-

[1] Seger's manometer may be used if a vertical form of instrument is desired.

[2] The anemometer was the property of the Department of Mechanical Engineering of Stanford University, and was the best instrument which could be purchased. The apparatus used for this purpose was designed for us by Professor W. R. Eckhart, Jr.

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anism could be turned on or off without removing the apparatus from its place. The Pitot tube (P) and the anemometer (M) were set so that their axes were at equal distances from the axis of the pipe. The whole

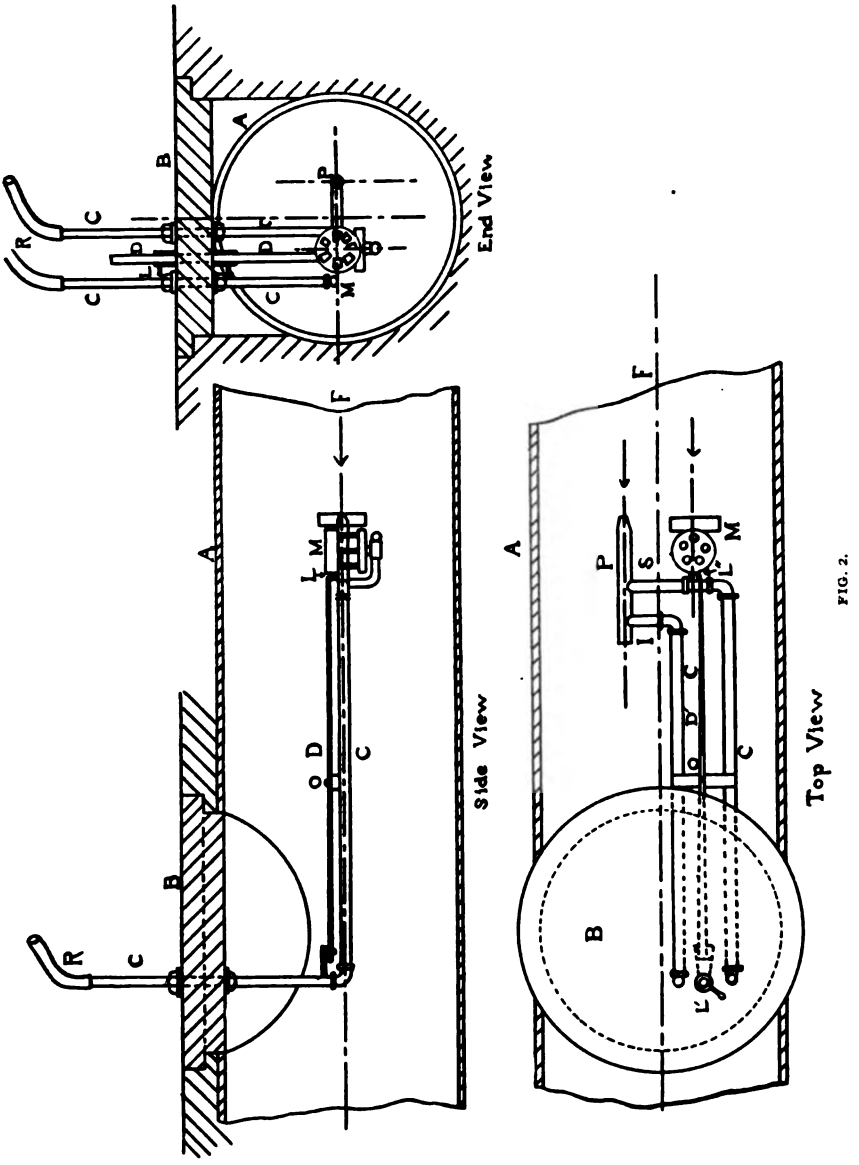


FIG. 2.

apparatus being supported by the tubes (C), which were fastened in the removable cover (B) of the manhole, could be removed in a moment to read the anemometer. The instruments were set several feet from

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the manhole so that the slight irregularities in the pipe at the latter would cause no eddies near the instruments.

The apparatus was put in place, and the fan regulated until the manometer of the Pitot tube indicated that the velocity of the air had become as nearly constant as possible. The recording mechanism was then turned on, and the readings of the Pitot tube manometer taken for a certain time, usually five minutes. The recording mechansim of the anemometer was then stopped, the apparatus taken out, and the dial read. The fan was run at the highest and lowest velocities possible, as well as at numerous intermediate velocities. The determinations as shown in Table 1[1], are not given in the order in which they were made, but are rearranged in the order of the increasing velocity.

The column "Ft. per Second Corrected" gives the results as determined by the anemometer, corrected by the calibration curve of the instrument maker. Under $\frac{V_{anemometer}}{V_{pitot}}$, the first column gives the anemometer velocity as obtained directly by reading the dial, divided by the velocity as determined by the Pitot tube. In the second column the anemometer reading has been corrected by its calibration curve.

On account of this rise of reading with the velocity, the easy corrosion of its parts, the fact that in the smoke the vanes become loaded with flue dust, and its high original cost, the wheel anemometer is a very poor instrument for the determination of the velocity of smelter smoke. The cost is of importance, since a number of instruments should be used.

Determination of the Velocity Curve.—The sampling hole, through which all our apparatus was introduced into the stack, was 5.75 inches in diameter, formed by an iron pipe extending through the five-foot wall, and projecting one foot on the outside of the stack. It was 53 feet from the ground, at an altitude of 5935 feet, and about 13 feet above the top of the baffle wall, which extends across the middle of the stack. At the time our measurements were made, we believed that the top of the baffle wall was very much lower than it really is, so at that time we were not able to understand why our curve of velocity showed a velocity considerably lower at the center of the stack than at four feet from the inner wall. The sampling hole was the highest opening in the stack, and also the only opening at this height, so that we were able to secure no other support for our apparatus than its walls. Not only the small size of this opening, but also its length, and the fact that it was round, made it difficult to insert, and keep vertical, any large amount of apparatus for the velocity determination. When no smoke sample was being drawn off, it was possible to insert four tubes for the

[1] The calculations in this table, and all the other calculations in this paper, were made on a slide rule.

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TABLE I. Comparison of an Anemometer and a Pitot Tube.

$$V_{Pitot} = \sqrt{2gh\,\frac{D_{ether}}{D_{air}}}$$

$2g = 64.28$ $b = 759$ mm $e = 12.7$ mm.

	Anemometer							Pitot.								
No.	2nd Reading Anemometer	1st Reading Anemometer	Difference	Time Minutes	Ft. per minute	Ft. per second	Ft. per second corrected	Pitot Manometer average	Pitot pressure in feet vertical	Temperature °C.	$1 + .003665\,t$	$\frac{.0012934}{1+.003665\,t} \times \frac{759-s/_{13.6}e}{760} \frac{D_{ether}}{D_{air}}$	$\frac{D_{ether}}{D_{air}}$	Velocity by Pitot $\frac{Ft}{Sec}$	V anemometer / V Pitot Readings	V anemometer / V Pitot Corrected
1	97,606	97,030	576	1	576.0	9.60	9.55	0.312	.00260	16.5	1.0605	.001209	603.0	10.03	0.957	0.952
2	101,108	97,606	3,502	5	700.4	11.67	11.55	0.383	.00319	15.8	1.0578	.001213	602.5	11.15	1.047	1.036
3	291,046	286,554	4,492	3	1497.3	24.95	24.45	1.547	.01289	22.0	1.0807	.001188	615.0	22.52	1.107	1.085
4	286,554	280,905	5,649	3	1883	31.38	30.75	2.320	.01933	22.0	1.0807	.001188	615.0	27.49	1.142	1.118
5	124,813	112,924	11,888	5	2377	39.63	38.84	3.437	.02864	18.4	1.0674	.001203	608.0	33.42	1.186	1.162
6	272,947	265,075	7,872	3	2624	43.73	42.86	4.375	.03646	22.5	1.0824	.001189	616.0	37.92	1.153	1.130
7	280,905	272,947	7,958	3	2653	44.22	43.34	4.445	.03704	22.5	1.0824	.001189	616.0	38.28	1.156	1.132
8	154,580	140,030	14,550	5	2910	48.50	47.54	4.954	.04128	20.8	1.0762	.001193	612.0	40.30	1.203	1.179
9	169,142	154,580	14,552	5	2910	48.50	47.54	5.023	.04186	20.8	1.0762	.001193	612.0	40.58	1.196	1.172
10	184,005	169,142	14,863	5	2972	49.53	48.54	5.198	.04332	21.3	1.0781	.001190	614.0	41.28	1.200	1.176
11	199,463	184,005	15,458	5	3092	51.53	50.50	5.682	.04735	22.8	1.0836	.001185	616.8	43 30	1.190	1.167
12	140,074	124,813	15,621	5	3052	50.87	49.84	5.940	.04950	21.1	1.0773	.001191	613.1	44 12	1.153	1.130
13	218,219	208,730	9,487	3	3162	52.70	51.65	5.922	.04935	22.8	1.0836	.001185	616.8	44.30	1.190	1.166
14	208,730	199,463	9,267	3	3089	51.48	50.45	5.917	.04931	23.0	1.0843	.001184	617.0	44.21	1.164	1.142
15	238,555	228,516	10,039	3	3346	55.77	54.66	6 813	.05677	22.8	1.0836	.001185	616.8	47.42	1.176	1.153
16	228,516	218,219	10,297	3	3432	57.20	56.16	6.877	.05731	22.8	1.0836	.001185	616.8	47.63	1.201	1.178
17	254,096	243,128	10,968	3	3656	60.93	59.71	7.553	.06294	23.0	1.0843	.001184	617.0	49 93	1.236	1.211
18	265,075	254,096	10,979	3	3659	60.98	59.76	7.677	.06397	23.4	1.0857	.001183	617.3	50.36	1.211	1.197

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determination of the velocity curve. The region near the wall of the stack is by far the most important in this determination. Thus one-half of the area of the cross section, with its radius of 15.67 feet, is within 4.66 feet of the wall, and also includes all that portion in which there is any great variation in the velocity. Measurements were made at the following distances from the inner wall of the stack, the numbers being given in feet: 0.0, 0.25, 0.50, 0.75, 1.0, 1.50, 2.00, 2.50, 3.00, 4.00, 10.00, and 15.67.

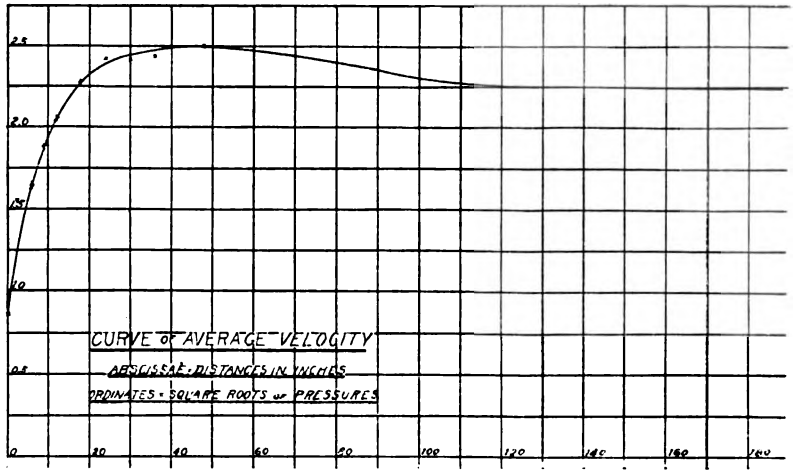


FIG. 3.

The results of these measurements are given in the form of a curve in Figure 3. Instead of plotting the velocities themselves, the square roots of the Pitot readings, multiplied by four, are given as ordinates, and distances from the inside wall as abscissæ. The extreme right of the curve represents the center of the stack. In computing the velocity for the time while samples of smoke were being taken for analysis, determinations were recorded at only one point, the point of maximum velocity, or four feet from the inside wall. This series of determinations was corrected by the velocity curve in order to give the average through the whole cross section. In computing this the method of sections was used. The radius of the stack was divided beginning at the center, into divisions of ten inches each; and the area of the ring formed by each segment, on rotating the radius in a plane about the center of the stack as an axis, was multiplied by the average velocity for that ring as shown by the curve.

Let $a = 10''$ $r_0 = 188''$ $r = 180''$ V = average velocity. Then since

$$V\pi r^2 = V_0\pi[188^2 - 180^2] + V_1\pi[r^2 - (r-a)^2] + V_2\pi[(r-a)^2 - (r-2a)^2] + \ldots\ldots\ldots\ldots + V_n\pi\left[\{r-(n-1)a\}^2 - (r-na)^2\right]$$

$$V = \tfrac{1}{r^2}[V_0(188^2 - 180^2) + a\{V_1(2r-a) + V_2(2r-3a) + V_3(2r-5a) + \ldots\ldots\ldots\ldots + V_n(2r-(2n-1)a\}]$$

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The calculation according to this formula is shown in Table 2.

TABLE 2

	V.	$2r-(2n-1)a$.	Product.	Product times a
V_0	6.00			17760.
V_1	8.40	350	2940.	29400.
V_2	9.53	330	3146.	31460.
V_3	9.83	310	3046.	30460.
V_4	9.95	290	2885.	28850.
V_5	9.92	270	2678.	26780.
V_6	9.77	250	2442.	24420.
V_7	9.53	230	2192.	21920.
V_8	9.31	210	1955.	19550.
V_9	9.18	190	1744.	17440.
V_{10}	9.08	170	1544.	15440.
V_{11}	9.01	150	1352.	13520.
V_{12}	8.98	130	1167.	11670.
V_{13}	8.96	110	986.	9860.
V_{14}	8.94	90	805.	8050.
V_{15}	8.93	70	625.	6250.
V_{16}	8.93	50	446.	4460.
V_{17}	8.93	30	268.	2680.
V_{18}	8.93	10	89.	890.
			Total =	320880.

$320880 \times \frac{1}{r^2} = \frac{320880}{35360} = 9.076$, or four times the average square root of the Pitot reading for the whole cross section of the stack. The average square root of the Pitot reading therefore = 2.269.

These measurements covered a period of eight and one-half hours. The average velocity corresponding to the average square root of the Pitot reading (2.269) is 55.80 ft. per second, which gives a volume of 3,721,000,000 cu. ft. in twenty-four hours under the conditions assumed to exist in the stack: temperature= 174.7° C, and pressure=612.2 mm. Under external conditions of t=17° C, and p=612.2 mm., the volume would be 2,411,000,000 cubic feet; and under standard conditions, 1,828,000,000 cubic feet. Although the results have been calculated to the same internal and external pressures, the external pressure exceeded the internal by about 5 mm Other tests will be given later which covered a greater period of time. The curve at 4 feet from the inside wall shows 9.95 as four times the square root of the Pitot reading. The average for the whole cross section of the stack, 9.076 divided by 9.95, the value at 4 feet, gives the factor 0.912. The average velocity over the whole cross section of the stack is therefore 0.912 of the maximum velocity, or the velocity at a distance of 4 feet from the inside wall. This factor is used later in converting velocity at this point into average velocity.

It had been planned to use sixteen tubes in the determination of the

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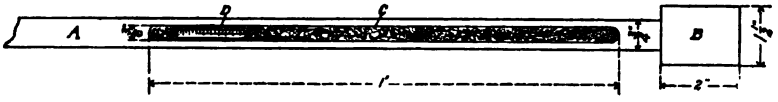
velocity of the smoke, but this method had to be abandoned on account of the small size of the opening through which the tubes were introduced. However, the arrangement will be described as it was planned, since it is a somewhat better method than the one we were forced to use. Sixteen tubes are placed in one cross section of the stack in the form of a spiral, each tube at an angle of seventy-two degrees from its neighbors on the spiral. On account of the much greater area of the outer rings when the cross section is divided into concentric rings of equal width, the greater part of the tubes should be near the wall of the stack. In order to obtain the true average Pitot pressure (h), allowance should be made for this fact by some method which depends upon the law, that the area of a circle is proportional to the square of its radius. If the radius is squared and this square divided into fifteen equal parts, the proper distance of the tubes from the center are found by extracting the square root of each of the numbers obtained in this way. For example, in the case of a stack with a radius of fifteen feet the numbers would be: 0, 15, 30, 45, 60, 75, 90, 105, 120, 135, 150, 165, 180, 195, 210 and 225. When the square roots of these numbers are taken, the distances of the tubes from the center are found to be as follows: 0, 3.87, 5.48, 6.71, 7.74, 8.66, 9.48, 10.24, 10.95, 11.62, 12.24, 12.83, 13.40, 13.95, 14.48, and 15. It would be even better to use nineteen tubes at distances of eighty degrees. All the tubes are connected through large air chambers (one for each arm of the manometer) to a differential manometer, or floating manometers may be used according to the method given by Captain Taylor. When this plan is followed, a mechanical average of the pressure through the stack is obtained, taking into account the greater area of the outer rings. The air chambers should be connected to the Pitot tubes so that there are separate connections provided with stop cocks for each tube. In this way readings may be taken on any one, or on all at the same time. The pressure given by the tube in contact with the wall of the stack is so low that it should not be connected with the manometer when the mechanical average is being taken, for it influences too greatly the pressure in the chambers. The greatest error in this method of obtaining a mechanical average is due to the fact that the average velocity obtained is not the true average velocity, but the square root of the average of the squares of the velocities. Still, the results obtained are so nearly correct that they are satisfactory for most purposes. If the relation between these quantities is desired, it can be determined by the apparatus as described above. Since the method would be obvious to a worker who could do work sufficiently accurate to need such a relation, only a bare outline of the procedure will be given. The readings of the separate tubes should be taken in order, one at a time, as rapidly as possible, and this procedure repeated a number of times. After each is

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read separately, a reading should be taken with all the tubes connected, except those that have not been included in the mechanical average. The single readings should then be calculated to velocity, and curves drawn showing its variation with the distance from the wall of the stack. From these can be calculated the average velocity by the method given later, or by any other satisfactory method. These results should then be compared with the results from the mechanical averages which were obtained under the same conditions. The ratio will serve for the correction of all the mechanical averages obtained during the drawing off of smoke samples. A simpler method would be to use the tubes singly in determining the velocity curve according to the method given by Figure 3 and the accompanying description.

Measurement of the Temperature.—The temperature was measured by the simplest means possible, which, while not so satisfactory as a good self-recording instrument[1], gave accurate measurements for the times that the readings could be taken. An accurate chemical thermometer was put in a long iron pipe A, Figure 4, with the bulb of the

FIGURE 4 Scale ½ Size



thermometer wrapped carefully in asbestos. The bulb was protected by an iron cap (B), two inches long and one and one-half inches in diameter. The whole stem of the thermometer, except the portion to be read, was wrapped in asbestos, and then the small exposed portion of the scale was covered with a loose layer of the same material. The scale of the thermometer could be read through a long slot (C) in the wall of the pipe. Before beginning the readings, the bulb (B) was put in the desired location in the stack, and left there for one hour. The pipe was then very quickly partially withdrawn, until the portion of the thermometer to be read (D) was just outside the sampling hole. This portion was quickly uncovered and the reading taken; then the scale was at once recovered and the instrument immediately inserted in the stack. Subsequent readings could be taken every fifteen minutes.

Velocity Measurements for the Smoke Samples.—Sample 4 was taken during a period of twenty-eight hours. Preparations had been made for a seventy-two hour run, but a violent thunderstorm stopped the work at the end of twenty-eight hours. The data and results of the velocity determinations for this sample are given in Table 3.

[1] A recording resistance thermometer may be used near the wall of the stack.

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TABLE 3.

VELOCITY OF THE SMOKE.

$$V = \sqrt{2gh\,\frac{D_{ether}}{D_{gas}}}$$

Density of Ether = c.7300

Density of Gas = 1.018 × Density of Dry Air.

	Pitot Reading.	Temperature.	*h* Feet	$D_{air\ dry}$	Velocity ft. per sec.=V
Aug. 23,'05					
A.M. 11.45	5.00	177	.04167	.0006312	55.05
12.45	4.75	177	.03960	.0006312	53.75
P.M. 1.45	5.25	173	.04375	.0006365	56.22
2.40	5.25	173	.04375	.0006365	56.22
3.00	7.00	173	.05833	.0006365	64.96
3.50	5.50	173	.04583	.0006365	57.60
4.30	6.00	173	.05000	.0006365	60.16
4.45	5.50	174	.04583	.0006350	57.64
5.00	6.50	177	.05416	.0006312	62.88
5.20	6.50	178	.05416	.0006298	62.96
3.40	6.25	174	.05208	.0006350	61.41
6.00	6.00	177	.05000	.0006310	60.43
6.10	7.00	176	.05833	.0006324	65.20
6.30	6.50	174	.05436	.0006350	62.76
6.50	7.00	180	.05833	.0006266	65.45
7.20	6.50	170	.05436	.0006406	62.52
7.55	7.50	172	.06250	.0006379	67.19
8.05	8.00	172	.06667	.0006379	69.40
8.20	8.25	176	.06867	.0006417	70.75
8.45	7.75	174	.06460	.0006350	68.42
9.15	7.00	173	.05833	.0006365	64.95
9.45	7.00	174	.05833	.0006350	65.00
10.00	7.00	174	.05833	.0006350	65.00
10.20	7.00	175	.05833	.0006329	65.13
11.15	6.00	180	.05000	.0006265	60.56
11.40	6.25	170	.05208	.0006409	61.16
A.M. 12.05	6.50	175	.05416	.0006329	62.75
12.15	6.50	180	.05416	.0006265	63.07
12.30	6.25	175	.05208	.0006329	61.54
12.50	6.50	174	.05416	.0006350	62.66
1.30	7.25	180	.06040	.0006265	66.70
2.00	8.00	175	.06667	.0006329	69.49
2.30	8.00	179	.06667	.0006283	69.95
3.30	7.00	174	.05833	.0006350	65.03
4.20	7.25	170	.06040	.0006409	65.86
4.45	7.50	171	.06250	.0006398	67.15
5.15	7.25	169	.06042	.0006423	65.82
5.45	7.00	165	.05833	.0006481	64.41
6.20	6.50	160	.05416	.0006557	61.65
6.40	6.00	158	.05000	.0006585	59.17
7.10	7.00	165	.05833	.0006484	64.41
7.25	8.00	166	.06667	.0006470	68.87

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Time.	Pitot Reading.	Temperature.	h Feet	$D_{air\ dry}$	Velocity ft. per sec. = V
8.05	8.50	173	.07083	.0006363	71.58
8.25	9.00	173	.07500	.0006363	73.65
9.20	8.50	175	.07083	.0006265	71.76
9.55	9.25	180	.07708	.0006329	75.22
10.45	9.50	185	.07916	.0006200	76.63
10.55	9.40	180	.07837	.0006265	75.84
11.05	9.40	180	.07837	.0006265	75.84
11.15	8.50	175	.07083	.0006329	71.75
11.20	9.50	175	.07916	.0006329	75.84
11.30	9.75	185	.08124	.0006200	77.64
12.00	8.75	178	.07294	.0006296	73.40
P.M. 12.25	9.00	177	.07500	.0006310	74.01
12.40	9.25	185	.07708	.0006200	75.65
1.00	8.75	183	.07294	.0006245	73.36
1.30	9.00	187	.07500	.0006175	74.78
2.00	8.50	171	.07083	.0006394	71.42
2.15	8.50	171	.07083	.0006394	71.42
2.32	9.00	180	.07500	.0006265	74.22

$g = 32.158$ Average Gas Pressure = 612.2mm.[1]

Pitot tube at 48 inches from the inside wall of the stack.

The average velocity was obtained by plotting the results given in this table as ordinates and the time in hours as abscissæ, which gave the curve shown in Figure 5. The average velocity was found by obtaining

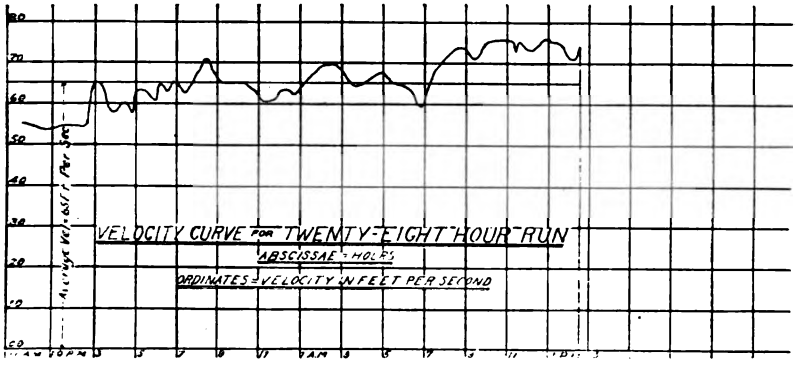


FIG. 5

the area of the curve with a planimeter, and dividing this area by the horizontal distance across it. The result obtained in this way is 65.00 feet per second. From this the average velocity for the whole cross section of the stack is 59.24 feet per second, or 65.00 multiplied by 0.912, the factor for conversion into average velocity, and the volume per day at the temperature of the stack, 3,098,000,000 cubic feet. At the temperature of 17° (the average temperature of the surrounding air) the volume would be 2,007,000,000 cu. ft., and under standard conditions, 1,523,000,000 cu. ft.

[1] On account of the breaking of our standard barometer during transit by express, an aneroid barometer had to be used in taking the pressures.

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The average velocity for smoke sample 2 was found in exactly the same way, the data being given in Table 4. On account of an accident to the velocity determination apparatus, there is a considerable break in the readings between 8.30 and 12 A. M.

TABLE 4 (Sample 2). -VELOCITY OF SMOKE.

July 23, 1905. $p = 613.4$ mm.

Time.	Pitot.	T.	h Feet	$D_{air\ dry}$	V.
A.M. 1.00	7.25	182	.06038	.0006264	66.64
1.15	7.00	182	.05828	.0006264	65.45
2.00	6.75	182	.05624	.0006264	64.34
2.50	6.50	182	.05414	.0006264	63.14
3.30	6.25	182	.05204	.0006264	61.84
4.10	5.50	182	.04580	.0006264	58.01
5.10	5.50	182	.04580	.0006264	58.01
6.10	5.25	182	.04372	.0006264	56.63
6.36	5.00	182	.04165	.0006264	55.36
8.30	4.75	181	.03957	.0006276	53.85
12:00	3.25	181	.02708	.0006276	44.58
P.M. 3.15	3.00	181	.02500	.0006276	42.85
3.35	3.20	181	.02666	.0006276	42.29
3.50	3.50	181	.02956	.0006276	46.28
4.00	4.00	181	.03332	.0006276	49.44
5.10	3.00	181	.02500	.0006276	42.85
6.00	2.50	181	.02092	.0006276	39.10
7.15	3.25	180	.02708	.0006294	44.57
7.50	4.00	179	.03332	.0006306	49.37
8.15	4.50	178	.03750	.0006308	52.34
8.45	5.00	177	.04163	.0006334	55 04
9.15	5.00	176	.04163	.0006346	55.03
9.45	4.50	175	.03750	.0006361	52.15
10.00	4.00	174	.03332	.0006376	49.10
10.25	4.50	174	.03748	.0006376	53.07

The average velocity as calculated from the curve, Fig. 6, is 50.90

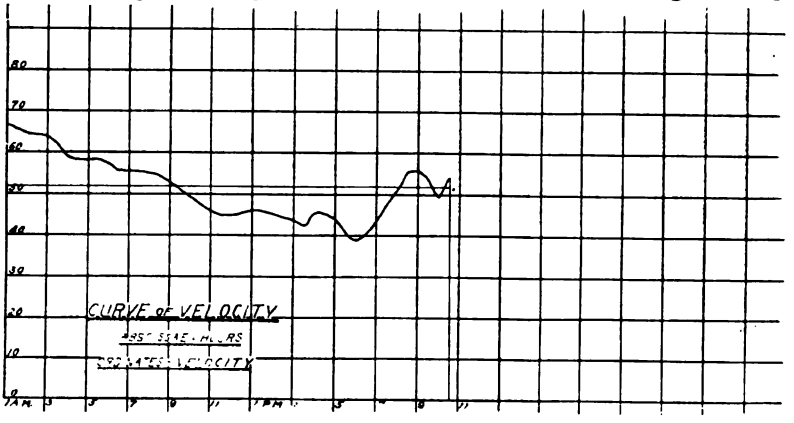


FIG. 6

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feet per second; this multiplied by the factor 0.912, gives the average velocity for the whole cross section of the stack as 46.43 feet per second. The volume at the temperature of the stack in cubic feet per day is 3,098,000,000; under the conditions of the outside air, 2,007,000,000; and under standard conditions, 1,523,000,000.

Another smoke sample was taken on July 27, 1905, the measurements being made four feet from the inner wall of the stack, and under an average pressure of 616 mm. The results of the velocity measurements are given in Table 5.

TABLE 5 (Sample 3).—VELOCITY OF SMOKE.

July 27, 1905. p = 616 mm.

Time.	Pitot inches	T	h Feet	$D_{dry\ air}$	v
A.M. 8.40	4.00	189	.0333	.0006187	49.80
8.55	4.00	189	.0333	.0006187	49.80
9.30	4.25	189	.0354	.0006187	51.38
10.00	4.50	189	.0375	.0006187	52.85
10.35	4.75	189	.0396	.0006187	54.32
11.10	4.75	190	.0396	.0006076	54.40
11.45	5.00	189	.0416	.0006187	55.63
P.M. 12.45	5.00	188	.0416	.0006292	55.58
1.30	5.00	187	.0416	.0006018	55.55
2.20	5.50	188	.0458	.0006202	56.44
3.10	4.75	189	.0396	.0006187	54.32
3.45	4.75	191	.0396	.0006148	54.46
5.00	5.25	189	.0437	.0006191	57.02
6.00	5.25	188	.0437	.0006292	56.98
6.15	5.00	187	.0416	.0006018	55.58

The average velocity is 54.86 feet per second, or 50.04 feet per second for the whole cross section of the stack. The volume of the smoke per day is 3,337,000,000 cubic feet at the temperature of the stack; 2,092,000,000 cubic feet at the temperature of the outer air (17°); and 1,595,000,000 cubic feet at standard conditions.

A summary and average of the volume determinations will be given later in the paper.

Standardization of the Meter.—A recording wet meter would have been used for this work if it could have been procured in time, but the best instrument available was of the type of dry meter used for measuring the volume of illuminating gas.

The great inconvenience of this type is that for small volumes it is necessary to keep track of the movement of the hand which gives the number of cubic feet and fractions, since the recording hands do not move with sufficiency accuracy. This is not so great an inconvenience as it seems, for in any case it is necessary to note constantly the velocity at which the smoke is passing through the sampling apparatus. The meter was tested by displacing the air from a large gas holder by the

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addition of water. Several tests were made in this way, the gasholder being connected with the meter, and the latter to a filter pump. The meter was tested at various pressures, the pressure in the apparatus being determined and kept constant by means of a T tube which was interposed between the meter and the gas holder. The lower arm of this T tube was graduated in millimeters, and dipped into a cup of mercury. In the later experiments the gasholder was replaced by a fifty gallon tank, into which measured amounts of water were introduced from a large carboy. The results are shown in Table 6.

TABLE 6.—AIR DRAWN THROUGH METER.

Test	Pressure.	Meter Cu. Feet.	Gasometer Cu. Ft.	Correction Cu. Ft.	Correction Per Cent.
1	580 mm.	14.25	14.44	+ 0.19	+ 1.31
2	430 "	22.00	22.32	+ 0.32	+ 1.43
3	500 "	16.00	16.19	+ 0.19	+ 1.17

The average correction of the meter reading was taken as 1.3 per cent. Experiments at pressures slightly over 760 mm. gave practically the same correction.

Apparatus for Collecting Samples of Solids.—In sampling smoke for solids there are a few general principles which should be observed in the design of the apparatus for the work. The apparatus recommended for this purpose is shown in Fig. 7, of which the apparatus used by us in our work is a modification. The gas should pass through the opening (O) of the sampling tube at the same velocity as that of the surrounding smoke, which may be as great as 75 feet per second, or 4,500 feet per minute, according to the data given in Table 3. The flue dust tends to collect to some extent around the edge of the opening (O), and if this is very small, may change the diameter so materially that it is difficult to calculate the velocity through it. If this factor alone were considered, the opening (O) would be made large; but, since the volume of the smoke which passes through the sampling apparatus varies as the square of the diameter of the tube, the practical limit must be small, unless the apparatus is made exceedingly large. The apparatus as shown in Figure 6 is intended for an opening 0.60 to 1.00 centimeter in diameter. When the opening is of this size, the apparatus must be large, if the velocities encountered are as great as those in our experiments. The tube (B) through which the smoke first passes after leaving the stack, is shown as eight centimeters in diameter, and the rest of the apparatus in proportion; though if convenient, it would be better to have this one tube (B) even larger.

In the case of sample Number 4, (A) was a Jena hard glass tube, 24 feet long, supported and protected by an iron pipe in which it was placed. A porcelain lined iron tube was tried in the case of sample 1 (which has not been given), but this was unsatisfactory as the porcelain

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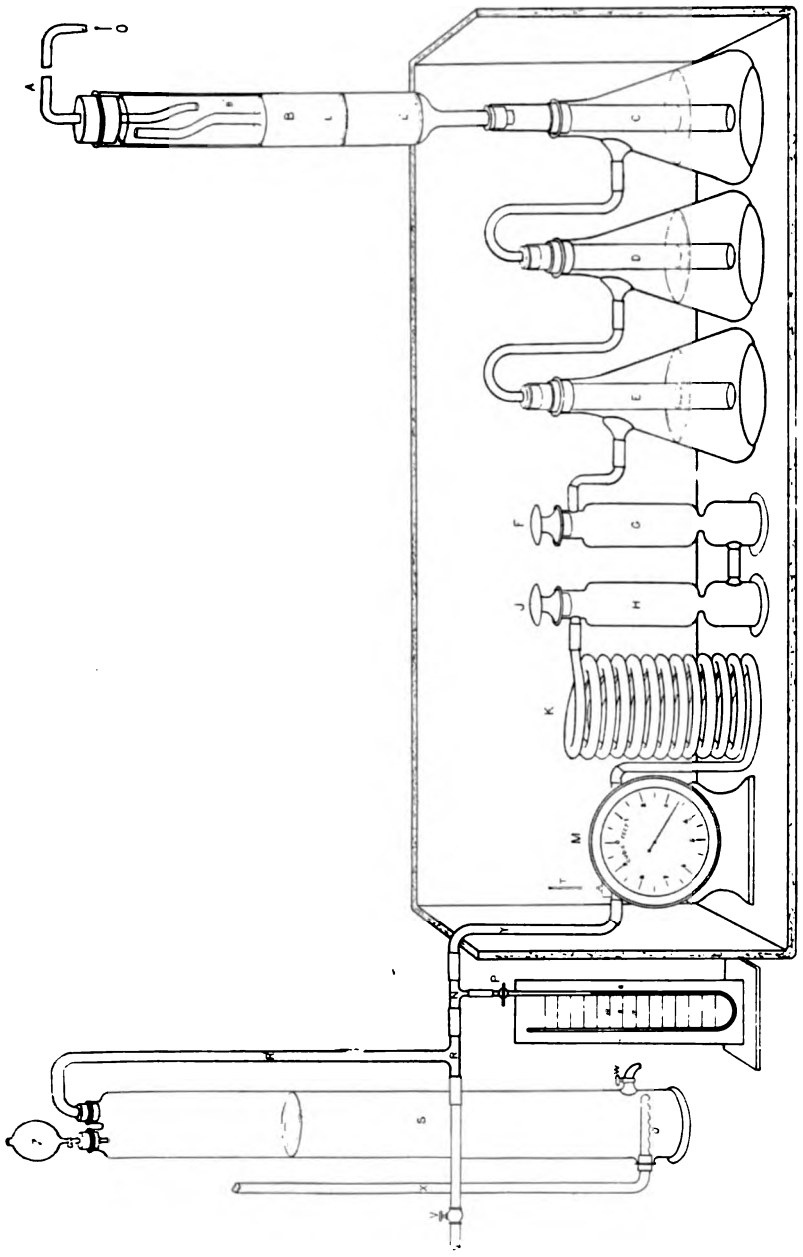


FIG. 7. Apparatus for Collecting the Solids of Smoke.

lining cracked. (B) is a large tube of thin glass, having projections on the inside for the support of other apparatus; B′, a glass cup[1], de-

[1] This is omitted, if the total weight of dust is not desired. A simple cup, without the inside tube, would serve as well and be less fragile. It is supported by platinum wires.

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signed to catch any heavy dust which may pass through the tube A; L and L′ are porcelain discs upon which ash free absorbent cotton is piled loosely. The gas next passes through three large filter flasks (C,D, and E), then through two bottles (G and H) filled with absorbent cotton; and finally, just before entering the meter, through a coil of thin copper tubing in order to equalize the temperature. This apparatus, including the meter, is contained in a box in which all the apparatus may be carried. The box is made water tight, so that water may be kept running through it in order to maintain a constant temperature. A window just in front of the dial of the meter, makes the reading of the latter easy, while a cover having openings for the tubes (B) and (Y), protects the apparatus while in use and during its transportation. After passing the meter, the gas is drawn off through an iron pipe. The pressure is partially regulated by the valve (V) in the pipe, and is measured by the manometer (Q), being finally determined by the height of the liquid (mercury or water) in the regulating tower (S). The exhaust through the valve (V) is always kept just strong enough to cause a small amount of air to pass down the tube (X), through the openings (O′), the column of liquid in (S), and the tube (R) into the T tube which forms a portion of the main exhaust pipe. Liquid may be added to the tower (S) by the dropping funnel (Z), or drawn off through the outlet (W). The three filter flasks contain water or some other liquid absorbent; and although not shown in the drawing, the lower portions of the tubes (C), (D), and (E), are pierced by a large number of small holes. The connections are made by rubber stoppers and by rubber tubes which have been first soaked in strong caustic potash solution, then in water, and finally in paraffin. Glass stoppers are not so satisfactory, since they sometimes begin to leak suddenly; and they weaken the apparatus, making it less flexible. Large rubber stoppers have the base covered by a disc of glass. Other parts may easily be added to the apparatus, such as a large trap to catch the solids just before they pass into B, in order to decrease the clogging of the absorbent cotton by dust.

It will be found, on using a properly constructed apparatus, that the greater portion of the heavy solids will deposit before reaching the absorbent cotton; however, it will be necessary to insert the trap in (A) if high velocities are to be used.

In our work we used a smaller opening (O) of the sampling tube, and found that in a short time the maximum amount of flue dust collected at its mouth, the high velocity at this point keeping it from filling up to any extent. Still, the larger opening is advised, since its free diameter can be calculated with more certainty. The opening should be of platinum foil, or of a sharpened glass tube. If it is desired that the mouth of the sampling tube should be placed in different portions of the cross section

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of the stack for different periods of the time of sampling, this may be accomplished by making the portion of the sampling tube (A) which lies outside the stack in several joints.

It will often be advisable to use the apparatus in a simplified form, in which case the tube (B) may be made from a condenser jacket simply filled with cotton. This was the form of apparatus used in the work given in this paper, and it proved very satisfactory. However, the glass tube (A) was so long that it rendered the use of a cup or a trap unnecessary, as will be shown by the data on Sample 4.

Determination of the Total Weight of the Solids.— In determining the total weight of the solids contained in a certain volume of the smoke, as great a quantity of the dust as is possible should be collected before the smoke reaches the absorbent cotton. Asbestos fiber may be used in the place of the cotton, but the latter is more efficient in stopping the finer particles. A large amount of the solids can be shaken out from the tubes (A) and the cup (B′) and weighed without further treatment. The whole inside of the apparatus should then be washed[1] with water, the solution filtered and evaporated. The residue from the evaporation and that on the filter paper (or better, in the Gooch crucible) is first dried and then weighed. The remainder of the solids may then be washed out by aqua regia, the solution evaporated, the residue dried and weighed. The cotton, which should be of a known weight and ash content and as ash free as possible, is decomposed by nitric and sulphuric acids until the organic matter is entirely destroyed, then the solution is evaporated, and the residue dried and weighed. Although a portion of the dust is changed somewhat in chemical composition by the action of the solvents, the results are sufficiently accurate. The total weight of the dust may be checked by a complete analysis of the residues.[2]

The Collection and Analysis of the Samples.— Sample 4, the velocity determinations for which are given in Table 3, was taken from the center of the stack through a tube (A) of Jena glass 23 feet in length and one-half inch in diameter, with a small opening (O) through which the smoke was drawn. The sampling was begun August 23 at 10.55 A. M., and continued, with an hour's intermission, until the next day

[1] To aid in the washing, the tube (A) may be cut into sections, and a glass rod with a rubber end used to loosen the adherent particles.

[2] The use of several large porcelain filters (six inches in diameter) has proved satisfactory in preliminary experimental work on the determination of the total solids. The first filters are covered with coarse, and the last with finely shredded asbestos. No liquid absorbent is used, but the tubes leading to the filters must be cleaned carefully. The weight is determined by direct weighing after drying. This method may be used where the more complex apparatus of our standard method is too cumbersome. Filter paper may be used for low velocities in cases where the smoke does not have a chemical action upon the paper.

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at 2.32 P. M. The total volume of the sample at 17° was 123.2 cubic feet, this being the meter reading, corrected for the error of the meter, and for the solubility of the gases in the absorbing liquid. Since in this case the opening (O) was so small that the sampling velocity did not need to be very great, it was decided to ascertain how much of the sample would deposit in the glass tube (A) (Figure 6). The tube (B) was omitted, but in its place, the tubes (C), (D) and (E) were fiilled with absorbent cotton. The velocity of the gas through the sampling tube itself was approximately one and one-half feet per second, the first fifteen feet of the tube from the opening having a temperature of 174.7° on the average, while in the remaining eight feet, the temperature fell gradually to about 25°.

The deposit in the tube was washed with water, and the water solution analyzed for arsenic, giving 0.009496 grams of arsenic trioxide per cubic foot, or 53,580 pounds per day of soluble arsenic trioxide for the portion of the sample which settled in the tube. The solution in the flasks was filtered, and the filtrate added to the water washings of the cotton. On analysis, this gave 0.001446 grams of arsenic trioxide to the cubic foot, or 8,200 pounds per day, which shows that 87.7 per cent. of the soluble arsenic was collected in the glass tube (A). The insoluble portions were analyzed together, and gave 6,000 pounds per day of water insoluble arsenic calculated as arsenic trioxide. This sample gave as a result, 61,780 pounds of water soluble arsenic trioxide; 6,000 pounds of water, insoluble; and a total of 67,780 pounds of arsenic trioxide per day as the amount sent out in the smoke.

In the case of Sample 2 (See Table 4 for the velocity determination), the sample was divided into two parts; the water soluble and the water insoluble. The sample was taken from a point four feet from the inner wall of the stack, beginning July 23, 1905, at 1 A. M., and stopping at 10.35 P. M. the same day. Of this time there were four hours during which the sampling apparatus was not running. The results of this test are shown in Table 7, which gives the results for the more impor-

TABLE 7.

APPROXIMATE AMOUNTS OF SUBSTANCES EXPELLED IN THE SMOKE, AS DETERMINED FROM SAMPLE 2.[1]

	Water Soluble.		Water Insoluble.		Total.	
Substance.	Grams per cu. ft.	Pounds per day.	Grams per cu. ft.	Pounds per day.	Grams per cu.ft.	Pounds per day.
Arsenic trioxide	0.01212	52,650	0.001428	6,204	0.01355	58,854
Antimony trioxide	0.000650	2,800	0 000321	1,400	0.000971	4,200
Copper	0.00071	3,100	0.00046	2,000	0.00117	5,100
Lead	trace		0.00110	4,800	0.00110	4,800
Zinc					0.0013	5,500
Iron and Aluminum Oxides	0.00318	13,800	0.00221	9,600	0.00539	25,400
Bismuth					0.00021	880

[1] Volume of smoke per day for Sample 2 = 2,007,000,000 cu. ft. under the conditions of the meter. Volume of sample (corrected) = 72.53 cu. ft.

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tant metals. Where only the total is given, the soluble and insoluble portions were united before making the determination.

The analysis of Sample 3 (velocity of determination, Table 5) is given in the form of a table of the same kind (Table 8).

TABLE 8.

APPROXIMATE AMOUNTS OF SUBSTANCES EXPELLED IN THE SMOKE, AS DETERMINED FROM SAMPLE 3, JULY 27, 1905.

Substance.	Water Soluble. Grams per cu. ft.	Water Soluble. Pounds per day.	Water Insoluble. Grams per cu. ft.	Water Insoluble. Pounds per day.	Total. Grams per cu. ft.	Total. Pounds per day.
Arsenic trioxide	0.00988	47,000	0.00089	4,210	0.01077	51,210
Antimony trioxide					0.00093	4,400
Copper	0.00058	2,700	0.00023	1,080	0.00081	3,780
Lead			0.00100	4,750	0.00100	4,750
Zinc	0.00137	6,480			0.00137	6,480
Iron and Aluminum Oxides	0.00109	5,280	0.00162	7,680	0.00271	12,960
Silica					0.00219	10,260
Manganese	0.000040	180			0.000040	180

Volume of Smoke per day under the conditions of the meter = 2,161,000,000 cu. ft. Volume of sample (corrected) = 72.40 cu. ft.

In obtaining the above results, standard analytical methods were used, the arsenic determinations being made, as a rule, in triplicate, using different methods. The arsenic and antimony were separated from the lead, bismuth, and copper, by the use of chemically pure sodium sulphide, using in each case a fresh solution. The arsenic was separated from the antimony by a fusion method, by distillation, or by precipitation of the pentasulphide in a strong hydrochloric acid solution, the last method being preferred. In this case the pentasulphide was first weighed in a platinum Gooch crucible, then dissolved in caustic potash, oxidized by chlorine, acidified with hydrochloric acid, the chlorine boiled off, and the arsenic finally precipitated in an ammoniacal solution as magnesium ammonium arsenate. The solution was then filtered through a platinum Gooch crucible, and the precipitate heated by a Bunsen flame, the platinum crucible being protected from too high a temperature by a large porcelain crucible in which it was placed. The antimony was precipitated as antimony trisulphide, filtered through a Gooch crucible, and the precipitate heated in a stream of carbon dioxide in a Paul's drying oven. The lead was determined as sulphate, and by electrolysis; the bismuth, separated by repeated precipitations with ammonium carbonate; and the copper determined by electrolysis.

Sulphur Dioxide. Five determinations of sulphur dioxide, made August 25, 1905, will be given here to show something of the amount of sulphur dioxide which is thrown off by the smelter. Other determinations were made at different times, but will not be reported, since there is some uncertainty due to a loss of a portion of the notes. The gas

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itself was drawn through tenth normal iodine solution, from ten to forty cubic centimeters being used for each test. The results were calculated from the formulas:

$$V_1 = \frac{V\,(B\text{-}w) \times 273}{760 \times (273 + t)} + 11.19 \qquad \text{where } B = 613.4,\ w = 14.4,\ t = 17^{\circ}C$$

$$\%\ SO_2 = \frac{1119}{V_1}$$

The results of these determinations are shown in Table 9, where the probable value is calculated from the formula, $r = 0.6745\sqrt{\frac{v^2}{n-1}}$ where r is the variation of the probable value from the determined average.

TABLE 9.—PERCENTAGE OF SULPHUR DIOXIDE.

No.	Volume sample.	Vol = 10 cc. 1.	V_1	Per cent. SO_2	v	v^2
1	2100 cc.	1050	790.2	1.417	— .076	.005776
2	900	900	679.0	1.648	+ .155	.024025
3	1020	1020	768.0	1.458	— 0.35	.001225
4	3815	953.7	718.2	1.558	+ .065	.004225
5	3225	1075	809.0	1.384	- - .109	.011881

Average per cent. by volume of $SO_2 = 1.493 \pm .0732$.

Gravimetric determinations of sulphuric acid were made on the remaining solutions, and the sulphuric acid determined by difference. The average percentage by volume was 0.114.

A summary of the volume determinations and analyses of the smoke, is given in Table 10, where all the results for volume are given as calculated to uniform temperatures and pressures. The results for sulphur dioxide are obtained by taking the average percentage, and calculating the amount for each volume as given for the separate volume determinations.

TABLE 10.--SUMMARY OF THE VOLUME DETERMINATIONS.

Sample.	Velocity ft. per sec.	Cu ft. per day at temp. of stack=174.7° p = 612.2 mm.	Cu. ft. per day at temp. surrounding air = 17° C.	Cu. ft. per day standard conditions.	Tons Sulphur dioxide per day
2	46.43	3,098,000,000	2,007,500,000	1,523,000,000	2,038
3	50.04	3,337,000,000	2,161,000,000	1,641,000,000	2,195
4	59.24	3,951,000,000	2,561,000,000	1,942,000,000	2,597
5	55.80	3,721,000,000	2,411,000,000	1,828,000,000	2,443
Average	52.89	3,526,800,000	2,285,100,000	1,733,500,000	2,318

AVERAGE IN POUNDS PER DAY OF SUBSTANCES THROWN OFF IN THE SMOKE.

Arsenic trioxide	59,270
Antimony trioxide	4,320
Copper	4,340
Lead	4,775
Zinc	6,090
Oxides of Fe and Al	17,840
Bismuth	880
Manganese	180
Silica	10,260
Sulphur trioxide	447,600
Sulphur dioxide	4,636,000

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These results show that while the great flue, previously described, may be fairly efficient in settling the copper from the smoke, still a considerable amount escapes, while the amount of arsenic given off is very great. The greater part of this arsenic is in the form of the trioxide, though the crystals are somewhat rounded. A small amount exists as the trisulphide, and in the form of complex minerals containing iron. No attempt was made to identify the latter, but, judging from the ore, there was undoubtedly some enargite present.

Samples of flue dust were taken from the big flue in August, 1905, beginning at the bottom of the stack, and sampling at approximately equal intervals to the bottom of the sixty foot flue, a distance of about 2,200 feet. The results of the analyses for copper and arsenic as given in Table 11, throw some light on the efficiency of the flue, especially when the results of the analyses of the smoke are also considered. The flue collects daily approximately fifty tons of dust, but it seems evident that the amount collected near the stack would be much less than that collected in the portion nearer the furnaces.

TABLE 11.—ANALYSES OF FLUE DUST.

Number.	Location.	Per cent. Cu.	Per cent. As_2O_3
1	Near foot of stack	4.64	26.06
2		5.23	22.00
3		5.85	16.40
4	Bottom of 120′ flue	5.89	12.62
5	Near top of narrow flue	6.33	10.32
6		7.37	8.85
7	Bottom of narrow flue	8.00	7.14

Dust collected from the outside of the glass sampling tube in the stack gave 25.7 per cent., and dust which dropped from the top of the stack, 25.63 per cent. of *soluble* arsenic calculated as trioxide.

The flue dust at the top of the big flue is roasted to produce commercial arsenic trioxide, but all of the rest is sent to the reverberatories and smelted for copper, so that the arsenic which it contains must in the end be eliminated in the smoke, excepting only that portion which goes into the reverberatory slag.

The amount of copper deposited is greatest at the bottom of the flue, just as would be expected, since the copper is not in a volatile state; but the amount of arsenic increases rapidly as the stack is approached. The flue evidently ends just where it is beginning to be very effective in the condensation and settling of the trioxide of arsenic, and the greater part of this substance passes out through the stack. However, even at the bottom of the sixty foot flue a considerable amount is deposited. It is evident that a large percentage of the oxide of arsenic which condenses to the solid state while in the flue, is carried along simply be-

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cause it is so fine that it will not deposit at the rate the gas is moving, 11.4 feet (3.47 meters) per second. Most of the crystals which were obtained in the stack, were from 0.006 to 0.020 millimeters in diameter, but collected together in larger masses. After withdrawing each sample of smoke the sampling tube (A) (Figure 6) contained considerable loose dust which ran high in arsenic, and on the walls of the tube there was always some of the trioxide which had crystallized from a vapor. The sulphides of lead, bismuth, and arsenic were deposited in definite rings on the walls of this tube. The flue collects the greater part of the heavy metals, but allows the most of the white arsenic to pass as a finely divided solid, and as a gas.

The General Effects of the High Stack.—The change from low stacks to a very high one, has given an excellent opportunity to observe the difference in their effects. The result of the change has been to decrease the amount of arsenic deposited near the stack, and to spread it over a greater area. On account of the higher specific gravity of the smoke, it tends finally to fall to the earth, even though it may first be carried to a very great height, often striking the ground at distances of from one to four miles. As a general thing, the sulphur dioxide is more dilute when it reaches the ground than it was in the case of the lower stacks. However, there is often a greater amount of damage done in certain valleys which were previously protected by the mountains, but into which the smoke can now drop. The trees on certain high mountain sides are also acted upon more than before, in some cases showing a streak in the forest where the current of smoke passes, while below this the damage is less noticeable; but usually the gas finally descends into some valley. At times, in a high wind, the smoke will come to the ground at the base of the stack; and the leaves of shrubs in the valley about half a mile from the stack, and 1000 feet lower than its top, show a very high percentage of arsenic.

On the contrary, in still weather, the smoke sometimes rises very high, and seems to be carried away at a great elevation. It is certain, at least, that on level land, near the stack, the action of the sulphur dioxide is less intense than before, and as a result it is easier to raise trees and vegetables. In spite of these beneficial results the building of a high stack cannot always be recommended. Such a case was that of the Keswick smelter, where the smelter lay in a low, narrow valley. The short stacks threw out smoke which killed practically everything within a mile and a half on the low land. This district would have been of little use had a high stack been constructed, and the result would have been to spread the injurious action over an undamaged area, only to protect that which was already ruined.

In order to determine to what extent the smoke was diluted before

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striking the ground, one sample of air taken at a distance of two and one half miles was analyzed for arsenic, and gave three thousandths of a milligram of the oxide to a cubic foot. In this case we were in the rapidly passing clouds of dilute smoke only about one fourth of the time. Another analysis at the same distance gave one part of sulphur dioxide to thirteen thousand parts of air. Analysis of cloths, snow, wood, grass, and other substances showed considerable quantities of arsenic: most on surfaces turned upward, slightly less on vertical sides facing the smelter, and very little on vertical sides facing away from the smelter. The arsenic in the smoke as shown by the analyses, was, in the three cases, 91.8 per cent. 91.1 per cent., and 89.4 per cent. soluble in water; and the arsenic in two samples of grass was 92.6 per cent. and 83.6 per cent. soluble in the digestive fluids of the cow. As a rule, the arsenic in the grass is less soluble than that in the smoke, since the rains wash away the more soluble portions. The subject of the deposition of the arsenic will be treated in detail in the second article of this series.

The concentration of the sulphur dioxide in the air of a smelter district is much more variable than in the great cities during the winter. In neither case, however, is much known of the actual percentages present. While the amount present in a concentration of even a few hundredths of a per cent, may easily be determined by absorption in iodine or potassium permanganate, no method is at present known for the determination of the minute amounts of sulphur dioxide present in ordinary or even city air. The best that can be done at present is to approximate the total amount of sulphur gases in the air. A great deal of work has been done upon this subject recently in the smelter regions of the west using a solution of sodium bicarbonate or sodium carbonate as an absorbent. It should be emphasized that such alkaline liquids are wholly unsuitable as absorbents for sulphur dioxide, since even a ten per cent. potassium hydroxide solution does not completely absorb this gas.

In cities, sulphur dioxide is present in the greatest quantities during the winter, when it can have little action upon plant growth. In smelter regions, the amount of sulphur dioxide in the air depends more upon the winds and the humidity than upon the season of the year. The highest results for sulphur gases in city air were obtained by Oliver, who drew London air through dilute hydrogen peroxide. The amounts obtained were as follows:

	Per cubic meter.		Parts per million.
Cloudy weather	1.9 mg, SO_3 =	1,52 mg. SO_2 =	1.17 SO_2
Light fog	2.9	= 2.52	= 1.95
Heavy fog	6.0	= 4.80	= 3.71
Yellow fog	7.2	= 5.76	= 4.45
Black fog	14.1	= 11.28	= 8.73

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A comprehensive treatment of this subject is given by Max Rubner.[1] The determination of the amount of sulphur dioxide in the smoke stream is much more simple, since the concentration of the gas is considerable. The principal difficulty where high stacks are in use is that the smoke stream shifts so rapidly that it is usually impossible to follow it. The best time for such a determination is at night, when the smoke often settles in a cloud in the valley.

Many interesting problems have arisen in this work which could not be solved on account of lack of time. It is possible that the flue dust, as assorted by the flues and chambers, would supply a good field for work on the rare elements. An analysis made several years ago gave 0.011 per cent. vanadium, 0.027 per cent. selenium, and 0.016 per cent. tellurium; while a qualitative examination for the ordinary elements showed, in addition, the presence of silver, lead, bismuth, copper, arsenic, iron, aluminium, manganese, zinc, barium, calcium, magnesium, sodium, ammonium, silica, water, sulphuric acid, chlorides, sulphides, sulphites, sulphates and a trace of organic matter. Other elements might have been present in traces. The dust from the flue near the stack, or in the stack itself, contains a considerable amount of concentrated sulphuric acid, while that from near the furnaces contains much less. To this latter, together with the arsenic with which it is associated, is probably due much of the spotting of leaves which is so common in smelter regions. This action of the flue dust is of far less importance than that of the sulphur dioxide[2] in affecting the growth of plants, in spite of some recent opinions to the contrary; but the arsenic of the dust may affect to a greater degree the value of the grasses, since it renders them poisonous.

In conclusion, we wish to express our special indebtedness to Dr. John Maxson Stillman, who has helped us very greatly in all of this work. We wish also to thank Captain D. W. Taylor for the design of the Pitot tube, Professor Robert Sibley for checking the calculations, and Professors W. R. Eckart, Jr., W. F. Durand, and Albert W. Smith, for aid, and for suggestions as to the determination of velocity.

THE UNIVERSITY OF MONTANA AND STANFORD UNIVERSITY, April 22, 1907.

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INJURY TO VEGETATION AND ANIMAL LIFE BY SMELTER FUMES.

BY J. K. HAYWOOD.

Received May 19, 1907.

Before taking up the subject of the actual injury to vegetation and

[1] Rubner, Archiv. für Hygiene, LVII, 323-378; LIX, 91-149.

[2] For a comprehensive bibliography on the subject of damage by smelter smoke see: Haselhoff und Lindau, Die Beschädigung der Vegetation durch Rauch, Leipzig, 1903; Schroeder, J. v., u Reuss, C., Die Beschädigung der Vegetation durch Rauch und die Oberharzer Hüttenrauchschäden, Berlin, 1883.

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animals by various smelter wastes a few words in regard to the wastes that might arise from a plant smelting sulphide copper ore, are necessary. Three wastes arise which may be injurious to vegetation or animals: First the sulphur contained in the ore is gradually given off during the various processes of smelting as sulphur dioxide which would have its injurious action on vegetation. Second, in case arsenic is present in the ores as it often is, notably at Anaconda, Mont., it is given off in the fumes from the smelter in volatile form and deposited on the surrounding land and crops, where it may be sufficient in amount to poison cattle browsing on pastures exposed to it, or living on hay cut from it. In case ores contain a considerable quantity of arsenic it is a common practice to recover as much of it as possible by passing the fumes through long cooling flues. This is done at Anaconda, Montana, where the fumes are passed through extremely long cooling flues, the condensed arsenic being obtained in the form of flue dust. Even under the best circumstances, however, some of the arsenic will escape from the top of the chimney along with the sulphur dioxide in the fumes. Third, the tailings from the water concentration of the ore are discharged into convenient streams; the slag is discharged in a finely divided form on a dump, and the "slime" is left in piles in the open air. Both of the latter are exposed to the percolation of any rain that might fall and the slag is also exposed to the action of the water discharged from the smelter. In consequence of the above the streams receiving the waste water from reduction plants, may contain a comparatively large amount of copper in suspension, and are apt to contain some copper in solution. If these streams are used for irrigation purposes, a possible source of injury to vegetation is to be taken into account in considering the action of the copper present on growing crops.

In the first case of this kind studied by the writer in the vicinity of Redding,[1] California, no complaint had been made of the injury from arsenic or from copper, so that the only problem considered was the action of sulphur dioxide fumes on the surrounding vegetation.

Although the results of this Redding investigation have been already published a resumé of the results obtained will be given, in order that the reader may understand further work that has since been carried out.

Injury to Vegetation by Sulphur Dioxide Fumes, near Redding, California. In carrying on this investigation it was first necessary to show whether or not sulphur dioxide was injurious to plant life, how small a quantity was injurious and through what organs of the plant such injury took place. Light is thrown on this subject by the work of foreign chemists. Freytag[2] showed that sulphur dioxide does not in-

[1] Bull. No. 89, Bureau of Chem., U. S. Dept. of Agr.

[2] Mitt. d. Konigl. landw. Akad. Poppelsdorf, 1869, 2.

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jure the plant through the roots, by watering wheat, oats and peas with large amounts of dilute sulphurous acid and noting that the plants neither wilted nor was their crop yield reduced. Von Schroeder and Dumont[1] by an investigation on pines made in 1896 showed that the injury to vegetation by sulphur dioxide is not by means of the roots but through the leaves, and that even extremely minute quantities of sulphur dioxide are injurious. In a later investigation they showed that on fumigating pines 109 times with 1 part of sulphur dioxide to 100,000 parts of air, great injury was inflicted and that on fumigating a number of pines 583 times with 1 part of sulphur dioxide to 1,000,000 parts of air, injury was also to be noted.

The details of the work of the writer on injury to Australian pines and young cow peas are given in Bull. 89 of the Bureau of Chemistry. It is only necessary here to mention the results obtained.

1st. Pine trees fumigated 6 times with 1 part of sulphur dioxide to 100 parts of air showed great injury. All of the needles were drooping and nearly all had turned yellow or brown.

2nd. Pine trees fumigated 9 times with 1 part of sulphur dioxide to 1000 parts of air were greatly injured in the same manner as the plants just described.

3rd. Pine trees fumigated 50 times with 1 part of sulphur dioxide to 10,000 parts of air were badly injured.

4th. Cow peas fumigated 18 times with 1 part of sulphur dioxide to 10,000 parts of air lost all their leaves and could not be revived although carefully watered and tended outside the fumigation chamber.

5th. Pine trees fumigated 50 times with 1 part of sulphur dioxide to 30,000 parts of air showed decided injury.

It was next necessary to show that treating plants with sulphur dioxide increased the sulphur trioxide content of the leaves so that it was present in larger quantities in the treated plants than in the untreated ones. As a necessary consequence of such an increase the sulphur trioxide content of the ash of fumigated plants would be apt to be higher than that on an unfumigated plant.

In the work of Von Schroeder and Dumont previously mentioned, where different parts of the plants were treated with varying strengths of sulphur dioxide the sulphur trioxide content of the treated plants was in excess of that of the control plants in every case, and the percentage of sulphur trioxide in the ash of the treated plants was higher than that in the ash of the control plants. The same was found to be true on making analyses of the plants fumigated by the writer. From the above results a method was at once suggested for determining whether trees around a smelter were killed by the fumes or died from other causes.

[1] Therander forstl. Jahrb., 1896, 46:1.

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The next step in the investigation was to see whether the dead and badly injured trees around the Mountain Copper Co.'s works near Redding, Cal., usually contained more sulphur trioxide than trees of the same species which stood close by in the same soil but were not killed. Of 25 pairs of trees examined in various directions from the smelter 80 per cent. contained more sulphur trioxide in the leaves of the injured trees than in the leaves of the uninjured ones, while only 20 per cent. showed the reverse. It was further shown that 80 per cent. of the injured trees contained a larger percentage of sulphur trioxide in the ash of the leaves than the uninjured trees.[1]

In a similar investigation in the vicinity of a zinc smelter at Lethmathe, Germany, reported in Haselhoff and Lindau's work on Injury to Vegetation by Fumes, one especially conclusive examination was made of the foliage of the surrounding vegetation. The worker here, instead of selecting the trees in groups of two from the same location, one injured and the other uninjured, took his injured trees from points near the smelter and his uninjured ones to compare with these from points much more distant from the smelter, but in the same direction. (Where this can be done the results are even more conclusive than the results obtained by the writer by his method, but unfortunately the rugged nature of the country in the vicinity of the smelter at Redding forbade the use of tion by Fumes, one especially conclusive examination was made of the 89 per cent. contained more sulphur trioxide both in the leaves themselves and the ash of the leaves of the injured trees than in the uninjured ones.

Three or four years later this same region around the zinc smelter was again examined and it was found, of 19 groups of trees examined all contained more sulphur trioxide in the leaves of the injured trees than in those of the uninjured ones.

It might be of interest to give some idea of the amount of sulphur dioxide given off by the plant of the Mountain Copper Co. each day. It was found that the ore contained about 41.5 per cent of sulphur and about 1,000 tons were smelted daily, so that approximately 748 tons of sulphur dioxide were given off into the atmosphere each day.

From this work in the vicinity of the smelter near Redding, California, the writer drew the following conclusions:

1st. Sulphur dioxide, when present in very minute amounts, kills vegetation.

2nd. Such injury shows itself by an increased sulphur trioxide content of the foliage.

3rd. The vegetation around the smelter for at least 3½ miles north, 9 miles south, 2¼ miles east, and 5 to 6 miles west, is greatly injured,

[1] For a full discussion of this subject see Bull. 89, Bur. Chem., U. S. Dept. Agr.

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and less severe injury extends even beyond these limits for a considerable distance.

Injury to Vegetation By Sulphur Dioxide Fumes Around Ducktown, Tennessee. The next investigation of injury to vegetation by smelter fumes carried on by the writer was in the vicinity of Ducktown, Tenn.[1]

Here again the only injury complained of was that due to the action of sulphur dioxide on vegetation, so only this problem was studied. The chemist in this investigation was accompanied by one of the foresters of the Department of Agriculture, and only samples of those trees were collected which the forester was reasonably sure had not died from insect pests, forest fires, crowding, or other common causes of forest destruction.

Before going into the discussion of the chemical analyses a short account of the general situation of the smelters and the condition of the surrounding vegetation as it appeared to the writer, would not be out of place.

Location of Smelters and Appearance of Surrounding Vegetation. Two smelters are involved, 1st, the smelter of the Tennessee Copper Co., and the Smelter of the Ducktown Sulphur Copper and Iron Co. These are situated in a valley about 7 to 10 miles broad and approximately 20 miles long, from 1 to 2 miles S. W. and S. E. respectively, of Ducktown. To the east, west, and north fairly high mountains separate this valley from the adjoining country. Toward the south the valley is gradually lost in the foot hills of adjacent mountains. At the northern end of this valley the Hiwassee River makes a cut through the mountains in approximately an easterly and westerly direction. At about the middle of the long diameter of this valley the Ocoee River, running in approximately a north westerly and southeasterly direction, flows across the valley and cuts through the mountains on the western side of the valley.

The direction of prevailing winds during the summer seems to be in a north westerly and south easterly direction. If the fumes are the cause of the destruction of the vegetation one would expect the greatest damage in this valley in the direction of the prevailing winds and in the cuts made by the rivers through the mountains. That such is the true distribution of the damage will be brought out later.

A careful general inspection of the country around the smelter shows that the area of very severe damage extends around the smelter in the form of an irregular ellipse, with its long diameter in a N.N.W. and S.S.E. direction, the total length of the long diameter is about 22 miles, and of the short diameter about 15 miles. The area of perceptible damage extends beyond the above area for a distance of 1 to 6 miles. A second trip was made to this affected area a year later than when the above

[1] The full details of this work will be given in a future bulletin of the Bureau of Chem. Only the principal results obtained are given here.

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observations were made, and it was found that severe damage could be noted in isolated areas about 20 miles south of the smelters.

In connection with this tour of observation, one point should be mentioned which came under the observation of the writer in a very forcible manner, and that is that different species of trees vary greatly in their susceptibility to sulphur dioxide fumes. For example, in the territory around Ducktown the white pines were injured or entirely dead when no other trees showed any injurious effect in the slightest degree. On the other hand, the post and white oaks and red maples were very resistant to the fumes and would grow very close to the smelter without seeming injury. Between these two limits were the Black, Red, Spanish, and Black Jack Oaks, and the yellow and scrub pines, which were neither so easily attacked as the former nor so resistant as the latter. A carefully arranged table was made out by the forester, showing in exactly what order the various species of trees were arranged as regards resistance to smelter fumes, but the above examples are sufficient for the present discussion. It might also be mentioned that individuals of certain species seemed to possess a certain immunity to the fumes and would grow some times within the area where it seemed impossible they could do so, but in the great majority of cases the divisions between the various species were perfectly apparent to a trained eye.

Having observed how far damage extended in the various directions from the smelters of Ducktown, samples were taken to prove or disprove that this injury was due to the sulphur dioxide given off. For this purpose, samples of the dead and injured trees surrounding the smelter were examined, as well as the uninjured trees of the same species beyond the range of apparent injury by the fumes. The sulphur trioxide content of the dead and injured trees was then compared with that of uninjured trees of the same species situated beyond the seeming area of damage. The soils of the injured trees were of course compared with those of the uninjured trees beyond the limit of damage to show that any increase that might arise in the sulphur trioxide content of the injured trees could not be due to an increased amount of sulphur trioxide in the soil.

If the sulphur trioxide content of the uninjured trees situated much farther away from the smelter, is less than that of the injured trees situated near the smelter, and yet the sulphur trioxide content of the soils in which the trees grow is the same, or nearly the same, in both cases, then this increase of sulphur trioxide in the injured tree must have been absorbed from the air. If the sulphur dioxide was so absorbed from the air, it must have been that which killed the trees, or at least helped to kill them, since we know that small amounts of sulphur di- and trioxide, when absorbed by the leaves of trees, kills them. In the absence of insect pests in sufficient numbers to cause great injury, of forest fires, and other or-

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dinary causes for the death of trees, we can only draw the conclusion that it was the sulphur dioxide only that killed them.

Attention should be here called to the fact that this method of comparing injured trees and uninjured trees is much better and more conclusive than the method followed by the writer at Redding, Cal., and should undoubtedly be followed in all cases where such comparison is possible. The country around Ducktown easily lent itself to carrying out the investigation in this way, while in the country around Redding, California, such a method of working out the problem was practically impossible. Of 49 such comparisons, in 46 cases or 94 per cent of the cases examined, the sulphur trioxide content of the injured trees was larger than that of the uninjured trees, at a greater distance beyond the range of seemingly significant damage.

In 82 per cent of the cases examined the sulphur trioxide content of the ash of the injured trees was larger than the sulphur trioxide content of the uninjured trees situated beyond the range of seeming damage.

Dividing these trees into 4 groups according to their direction from the smelter we have the following results.

In a northerly direction in 100 per cent of the cases examined the leaves of the injured trees contain a larger percentage of sulphur trioxide than the leaves of the uninjured trees, and in 81 per cent of the cases examined the ash of such injured trees contains a larger percentage of sulphur trioxide than the ash of the uninjured trees.

In an easterly direction in 100 per cent. of the cases examined the leaves of the injured trees contain a larger percentage of sulphur trioxide than the leaves of the uninjured trees, and in 75 per cent. of the cases examined the ash of such injured trees contains a larger percentage of sulphur trioxide than the ash of uninjured trees.

In a southerly direction in 77 per cent of the cases examined, the leaves of the injured trees contain a larger percentage of sulphur trioxide than the leaves of the uninjured trees, and in 69 per cent of the cases examined the ash of such injured trees contains a larger percentage of sulphur trioxide than the ash of uninjured trees.

In a westerly direction in 100 per cent of the cases examined both the leaves and the ash of the injured trees contain a larger percentage of sulphur trioxide than the leaves of the uninjured trees.

From the above investigation in the vicinity of Ducktown, I would draw the following conclusions in regard to the distribution of injury by the smelter fumes:

1st. That the vegetation around the smelter appears from actual chemical analysis to be injured for at least 10½ to 11 miles north of Ducktown, 8 miles south, 5 to 5½ miles east and 8½ miles west, (down the Ocoee River).

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2nd. That there can be but little doubt that the injury extends beyond the limits mentioned in (1), but it cannot be shown by chemical analysis since the difference in sulphur trioxide content between injured and uninjured trees becomes so small as to be within the limits of experimental error.

Investigation in the Vicinity of Anaconda, Mont. A third extremely important study of injury to vegetation and animals by smelter wastes is now being carried on by the writer in the country surrounding Anaconda, Montana. Here the huge smelter of the Amalgamated Copper Co. is situated, roasting, when running at full head, about 10,000 tones of ore per day. This ore is said to contain quite large quantities of arsenic. This smelter is situated in a semi-arid country, where irrigation is practised, the smelter discharging its wastes into certain of the streams that are used for irrigation purposes. There are therefore 3 distinct problems to be worked out in connection with the injury by the smelter.

1st. Whether or not the vegetation is injured by reason of the sulphur dioxide set free.

2nd. Whether or not enough arsenic is set free to settle on the surrounding vegetation and poison the forage plants so that they are unfit for cattle.

3d. Whether the waste when discharged into the irrigation streams, renders the water unfit for irrigation purposes.

The writer has started a study of all of these problems and has obtained enough data to draw tentative conclusions, but the work is still going on, and final results cannot be reported till later.

A few words of introduction are necessary in regard to the situation of the smelter, the appearance of the surrounding country and the injury claimed by the farming community in the vicinity of the smelter.

The smelter is situated on a high hill toward the southern end of Deer Lodge Valley, which is about 35 miles long and 4 to 6 miles wide. It is nearly at the junction of Deer Lodge Valley and Hot Springs Creek Valley. To the north, south, east and west of this valley are quite high ridges of mountains which are cleft here and there by the valleys of small creeks, Hot Springs Valley being one of the largest ones. Down the center of the Deer Lodge Valley runs Deer Lodge River into which are carried the tailings from the smelter. As I have said before, this river is used for irrigation purposes, although a large number of the farmers say that it is injurious and prefer to get their water from small creeks coming down from the mountains on either side, and only use the Deer Lodge River when it is absolutely necessary. The country immediately surrounding the smelter and in the Deer Lodge Valley proper, has never been wooded at all. It is only when we get toward the tops of the ridges and along the valleys of the various small streams and beyond the ridges

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that the land is forested to any extent. Besides this, forest fires have swept over certain of the mountains in the past, so that all dead timber cannot be ascribed to sulphur dioxide from the smelter. However, enough trees are present within a radius of 10 to 15 miles from the smelter, which have not been injured in any way by the forest fires, crowding, insect pests, etc., to be able to judge what the extent of the damage by sulphur dioxide has been and is. The three principal species of trees in the neighborhood of the smelter are the Lodge Pole pines, Junipers, and Red Firs. The difference in their resistance to sulphur dioxide fumes is very marked and can easily be observed by any one who chooses to drive over the country.

Trips were made by the writer and a forester for about 20 miles north, 10 miles south, 15 miles west and 6 miles east. Immediately surrounding the smelter practically all trees are either dead or severely injured. A very few trees still stand, to which those who do not believe in the injurious effects of smelter fumes point with pride as being examples of the fact that sulphur dioxide does not injure vegetation. Since, however, hundreds of the same kind of trees are killed outright at 10 times the distance away of these uninjured trees, the force of the argument is entirely lost and the uninjured trees only appear to a disinterested party as curious examples of individual resistance.

On the whole a careful examination shows that the forests are evidently injured for at least 14 miles north, an indefinite distance east, 8 miles south and 13 to 15 miles west (up Warm Springs Creek). The injury to Lodge Pole pines does not extend this far but the injury to Red Firs evidently does. Samples of injured foliage near the smelter and of uninjured foliage beyond the range of seeming smoke damage were collected just as in the case of the Ducktown region. The results of this work are not yet completed, but 12 comparisons have been made of injured samples collected in a southerly and westerly direction from the smelter with samples of the same species of trees collected beyond the range of seeming smoke injury. In eleven of these cases or 92 per cent the injured leaves contained more sulphur trioxide than the uninjured ones.

The next claim made by the farmers and requiring investigation, is that enough arsenic is given off from the stacks of the smelter to settle on the surrounding forage crops and so poison the cattle. To prove this it is first necessary to show that the ores smelted at this smelter contain arsenic. Examinations of three samples of ore, taken personally from three different mines which partly supply the smelter, were made and the following amounts of arsenic obtained: 0.51 per cent; 1.17 per cent; and 2.54 per cent. Of course a large amount of this is condensed by the condensing flues used at the smelter, however a larger or smaller quantity undoubtedly escapes from the chimney. It is next necessary to show that the escaping

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arsenic settles on the surrounding forage crops in large enough amounts to be injurious to cattle. For this purpose about 20 samples of range grass and such cultivated crops as alfalfa were collected for distances varying from 1 to 10 miles from the smelter in various directions, but more especially down the Deer Lodge Valley. Ten of these examinations have been made and the results given below obtained. The arsenic was determined by first destroying the organic matter with arsenic free nitric and sulphuric acids and then determining the arsenic by means of arsenic mirrors, using a modification of the Sanger method. [1]

Arsenic Content of Forage.

Description of Samples.					Mgs. of As. per. g. of dry sample.
Bunch Grass	2 miles	N.	Smelter		0.078
Alfalfa	2½ "	"	"	Supposed to have killed cattle	0.052
Pasture "	3 "	"	"		0.052
Red Top "	4 "	N.	E. "		0.021
" " "	5 "	N.	E. "	Supposed to have killed cattle	0.042
Alfalfa	10 "	N.	E. "		0.053
Bunch Grass	3 "	E.	"		0.032
Field "	6 "	E.	"	Supposed to have killed cattle	0.042
Hay	6 "	E.	"	" " " " "	0.031
Bunch Grass	6½ "	W.	"		0.042

From the above table it will be noted that arsenic was found in considerable quantities in every sample examined. Calculating this arsenic to a ration of 20 pounds of the dry forage we find in the case of the forage containing the least arsenic it amounts to about 3 grains per day, while in the case of the forage containing the largest quantity of arsenic it amounts to about 10.9 grains per day. It may be seen from the above that in order that the cattle in this region live at all they must become confirmed arsenic eaters, in much the same way as the mountaineers of Switzerland. Through the courtesy of Dr. D. E. Salmon, the writer was able to examine sections and gross specimens of the viscera of a number of cattle that were suspected of having been killed by eating forage containing arsenic as above. It was noted that the gastro intestinal tract was inflamed and the glands of the stomach and the kidney on section showed desquamation of epithelium, cloudy swelling and in some cases fatty degeneration. The symptoms described by the farmers include inflamation of the mucous membrane of the upper air passages, running from the nose, and incoordination of gait. From the above symptoms and post mortem appearances together with the amount of arsenic found in the various forage plants, there can be but little doubt that the cattle were killed by arsenic.

The third point claimed by the farmers and needing investigation, was

[1] A description of the apparatus used is given in Bull. 86, Bur. Chem., U. S. D.pt. of Agr.

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the injurious effect of the Deer Lodge River Water on farm crops when used for irrigation. It is evident from an inspection of the Deer Lodge River that tremendous quantities of waste matter from the plant finds its way into the stream. It is also evident from the method of operation that these waste products must contain some copper. This copper is to a large extent in the form of finely divided copper sulphide, which we know in nature forms soluble copper sulphate by gradual oxidation. We would therefore expect that if this material were put on the land it would gradually oxidize to a soluble form in which condition even very minute quantities of it would be more or less injurious to vegetation. It has been urged that even if soluble copper were formed in the Deer Lodge River or subsequently on the land it would be immediately rendered insoluble again by the action of carbonates and bicarbonates present in the water and soil. On the surface this looks plausible, but Skinner[1] has shown that such is not the case, but that when soluble copper salts are brought in contact with solutions containing carbonates and bicarbonates enough copper still remains in solution to be toxic to plants.

Samples of the waste water, from the plant, from the Deer Lodge River just after the waste was emptied into it, and from the Deer Lodge River at various distances from the point of inlet of the waste, were taken and the insoluble and soluble copper determined.

The following results were obtained:

Copper Content of Water Samples

Description of Samples	Insoluble Copper parts per million	Soluble Copper parts per million
Waste water of smelter	31.0	0.05
Deer Lodge River, 1½ miles below entrance of smelter waste	12.1	0.77
Deer Lodge River 6 miles below entrance of smelter waste	12.0	0.15
Deer Lodge River 8 miles below entrance of smelter waste	6.4	0.22
Deer Lodge River at Deer Lodge, about 16-18 miles below entrance of smelter waste	3.1	0.51

It is evident from the above that the plant discharges large quantities of copper into the Deer Lodge River and that even at a distance of 16 to 18 miles below the point where the tailings are discharged, a considerable quantity of copper is still present. Since it has been proven by Heald[2] that seedlings of Pisum Sativum are killed when the solution contains 1 part of copper in 404,423 parts of water and that Zea Mais seedlings are killed in a solution containing 1 part of copper per 808,846 parts of water; since it has further been proven by other investigations that even smaller quantities of soluble copper than the above are injurious to plant life; it would appear that the Deer Lodge River water even at a distance of 16 to 18 miles below where the tailings are discharged, is not fit for

[1] Copper Salts in Irrigation Waters. This Journal 27, (1906).
[2] Botan. Gaz. 22, 142.

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irrigation purposes, and will eventually if not at once seriously injure land to which it is applied.

To further prove that land irrigated by the Deer Lodge River contains excessive amounts of copper, samples were taken at various distances from the smelter with the idea of determining in them both soluble and insoluble copper. Several of these have been examined but the results show such excessive amounts of copper that the writer is not willing to publish the results until he has confirmed them by collecting and examining new samples. That considerable quantities of copper are present in this soil, however, is undoubtedly true since the soil along the edges of the irrigation ditches, 12 miles and more below the inlet of the smelter waste into the river, is colored distinctly blue with copper. Further than this, the writer tested the soil on a farm irrigated by the Deer Lodge River water 10 to 12 miles below the inlet of the tailings, with his knife blade and was able to obtain an excellent coat of what afterwards on examination proved to be copper.

Although the results of the examination of the injury to vegetation and animals by the Anaconda Smelter is not completed, from the work already done the following definite conclusions can be drawn.

1st. The vegetation around the smelter for at least 7 to 8 miles south and 13 to 15 miles west is seriously injured.

2nd. The Junipers are very resistant to smelter fumes and appear able to grow close to the smelter; the Red Firs are very susceptible to the fumes and are badly damaged at distances of 13 to 15 miles from the smelter; Lodge Pole pines are intermediate between the other two species of trees, but show damage for at least 10 miles.

3rd. Large quantities of arsenic are discharged from the smelter on the surrounding country, being present in forage crops in large enough quantities to poison cattle.

4th. The waste from the reduction plant discharged in the Deer Lodge River renders it unfit for irrigation purposes.

A PORTABLE PHOTOMETER.

By James A. Evans.

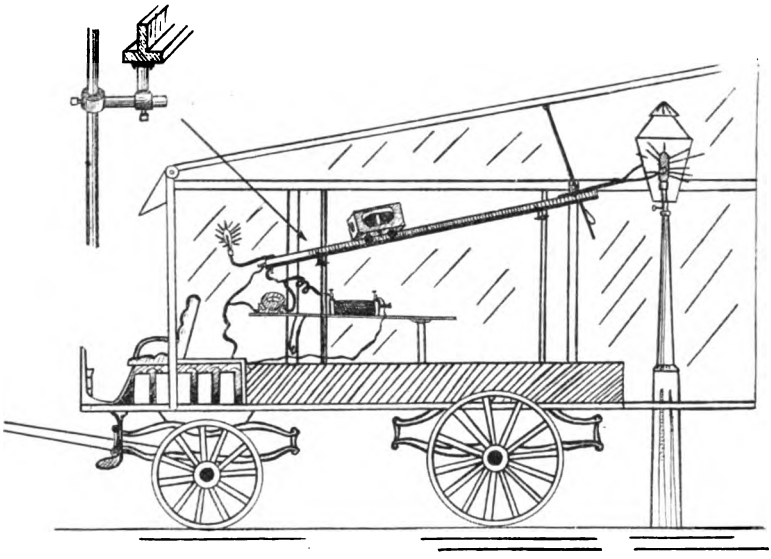
Received May 11, 1907.

During the years 1901 and 1902 the writer was Gas Inspector for the city of Cleveland, Ohio. During that time it became very urgent to know in concrete numbers what candle power the street lamps were producing, because the contract for street lighting was given on the basis of a definite candle power, with a penalty for falling below the specified standard.

The lamps were mantle burners with glass chimneys and enclosed in glass globes. They were fed by artificial gas and by gasoline. We

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first tried the portable photometers on the market, but they were entirely inadequate. The plan of transporting the lamps to the stationary photometer in the City Hall was tried, but the frail mantles were broken in transit and gave very erroneous results. I therefore invented the following Portable Photometer, which proved highly satisfactory.



A light spring wagon was secured and an adjustable top built on it. The frame was made of light steel and covered with oilcloth, which was painted a dead black on the inside, thus forming a veritable dark room. The frame work extended about four feet beyond the back end of the wagon, the roof was hung on hinges, at the front end, while the back end could be raised during operation, to take in the street lamp. The wagon was backed up to the curb and the lamp enclosed within the extension. A black oilcloth curtain was then drawn across the back, thus completing the dark room. Within the wagon, the photometer bar rested on round steel rods which were, in turn, attached to the upright pieces of the wagon top, giving place for the operator on the floor of the wagon. The bar was held in place by sliding set screws and could be moved out or in and up or down very conveniently and brought into perfect alignment with the light. In the front end of the wagon, under the seat, was a storage battery of 12 cells, with lead plates and dilute sulphuric acid for the electrolyte. An 8 candle power incandescent lamp was attached to the forward end of the bar and connected with the storage battery. In the circuit was a Weston voltmeter and rheostat. The lamp was standardized in the laboratory, from time to time, to find the exact voltage required to deliver exactly 8 candle power, and this volt-

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age was held constant when at work by means of the volt meter and rheostat. The bar was of wood and carefully graduated to sixteenths of an inch. Its base served as a track for the Lummer-Brodhun sighting box to run on. The bar was 8 feet long with the electric lamp at zero. The distance from the other end of the bar to the street light was measured by means of a light stick, with a pointer at one end of it and a fork at the other, large enough to span the lamp. Each prong of the fork terminated with a ring with a wire cross-hair stretched across it. This afforded an easy and accurate means of getting the distance from the center of the mantle to the end of the bar, which of course, varied with the different lamps.

The instrument required two men to operate it; one to adjust the bar and take the reading and the other to line up the cross hairs with the mantle and get the distance from the bar. The time required to back up to a lamp, adjust the bar, take the readings and measurements and get away was about seven minutes. The candle power of the lamps for each night's work was figured out afterwards by means of logarithms and a table of squares.

Erie, Pa.

CONTRIBUTIONS TO THE CHEMISTRY OF THALLIUM, II.

BY L. F. HAWLEY.

Received May 2, 1907.

A New Method for the Gravimetric Determination of Thallium. By precipitating and weighing the thallium as thallium sulphostannate, Tl_4SnS_4[1], a very accurate and easy determination of thallium can be made. The thallium sulphostannate can readily be prepared in pure condition; it is practically insoluble in water so that it can be washed very thoroughly without loss, and it can be dried at 105° without decomposition. The thallium may be in either the thallous or thallic condition at the time of precipitation since the precipitants will also act as reducing agents. All the elements precipitated by sodium sulphide, including those which are soluble in excess, will interfere with the formation of pure thallium sulphostannate. The reagents required are a solution of primary sodium sulphide with a concentration of about 150 grams per liter, and a solution of sodium sulphostannate containing only a slight excess of sodium sulphide. This latter solution need not be free from the sodium salts formed in its preparation and can therefore readily be made by adding sodium sulphide solution to a solution of stannic chloride until the precipitate first formed is just dissolved. The procedure for the preparation of the pure thallium sulphostannate is as follows:

To the hot and very slightly acid solution of the thallium salt add an excess of the sodium sulphostannate solution, *i. e.*, more than enough to form

[1] Hawley, J. Physic. Chem., 10, 654 (1906).

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Tl_4SnS_4 with all of the thallium present. The precipitate now consists of Tl_4SnS_4 and the solid solution with excess of stannic sulphide[1]; if the solution is still acid there is also some thallium unprecipitated. Add the primary sodium sulphide solution drop by drop with constant stirring until the solution is neutralized, then add at once 25 cc. more and heat to boiling. Boil slowly for five minutes, stirring with a rod held against the bottom of the beaker to prevent bumping. This boiling in the presence of the primary sodium sulphide solution dissolves any stannic sulphide in excess of the formula Tl_4SnS_4. A slight decomposition of the thallium sulphostannate into thallium sulphide and soluble stannic sulphide, amounting to a loss of from two to three milligrams as stannic sulphide may take place on boiling as above, but on diluting the solution with water and allowing it to stand for two or three hours, stannic sulphide is again taken up and the precipitate finally consists of pure thallium sulphostannate. This precipitate is filtered in a Gooch crucible, is washed with water, dried at 105°, and weighed. Determinations of the thallium in pure fused thallous sulphate prepared as in the previous article gave 80.96, 80.97, 80.90, 80.96, 80.93, and 80.94 per cent. of thallium. Tl_2SO_4—80.95 per cent. of thallium. The determination of thallium in 20 cc. portions of a thallic chloride solution gave by direct precipitation with sodium sulphostannate and primary sodium sulphide 0.9012 gram and 0.9010 gram Tl_4SnS_4, while by precipitation after reducing with sulphur dioxide and boiling out the excess there was obtained 0.9011 gram and 0.9008 gram Tl_4SnS_4.

Thallous Sulphide and Arsenic Trisulphide. Gunning[2] has described the precipitate formed between arsenious and thallous salts when treated with hydrogen sulphide in alkaline and in acid solutions. The composition of the precipitates varied widely with the methods of preparation and it was admitted that the substance did not seem to be a well defined chemical compound, yet the formula $TlAsS_2$ was given to it and it has gone into the literature as a compound of that composition. When such precipitates, obtained in either acid or alkaline solution, are examined under the microscope, they are found to be perfectly homogeneous for all compositions between pure arsenic trisulphide and about 62 mol. per cent. arsenic trisulphide. The color varies gradually from the light yellow of arsenic trisulphide through orange to a bright red as the amount of thallous sulphide increases. At about 62 molecular per cent. arsenic trisulphide, a second phase appears, the black thallous sulphide, and from that point to pure thallous sulphide two phases are present. These observations show that thallous sulphide and arsenic trisulphide under the conditions named form a limited series of solid solutions extending from pure arsenic trisulphide to about 62 molecular per cent. arsenic trisulphide

[1] Hawley, loc. cit.

[2] Chem. News, 17, 138 (1868); Arch. neerland. sci. exact. nat., 3, 86.

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and that no compound is formed. From these precipitates acids will dissolve more or less thallous sulphide, depending on the concentration of the acid and the composition of the precipitate. Likewise solutions of alkaline sulphides will dissolve out varying amounts of arsenic trisulphide. The nearly constant composition of some of Gunning's precipitates obtained in acid solution with excess of thallium present was probably due to the nearly constant concentration of the acid used. realgar from Allchar, Macedonia. This mineral occurs in well formed crystals and is apparently a later formation than the realgar. One analysis

A mineral lorandite, has been described by Krenner[1] as occurring on a only is on record and this agrees with the formula $TlAsS_2$, but in view of the fact that a series of solid solutions extending on either side of that composition are known to exist, it is probable that other analyses would show different compositions. It is possible, of course, that under different conditions of formation, as with heat, pressure, or absence of water, a definite compound might be formed which did not exist under the conditions of preparation used above.

Thallous Sulphide and Arsenic Pentasulphide. When thallium salts and pentavalent arsenic salts are precipitated together by alkaline sulphides precipitates containing thallous sulphide and arsenic pentasulphide are obtained which vary in color and properties according to the composition. Microscopic examination of these precipitates showed the phases present. From pure arsenic pentasulphide to the composition corresponding to $3\ Tl_2S.AsS_5$ there were two phases distinguishable, the light yellow arsenic pentasulphide and a more crystalline orange colored phase. At the composition $3\ Tl_2S.As_2S_5$ only the one orange colored phase was present but from that point to pure thallous sulphide the orange colored phase and the black thallous sulphide were present. These observations show that under the conditions given thallous sulphide and arsenic pentasulphide form a compound Tl_3AsS_4 but no solid solutions are formed. The same substances are formed by precipitation of thallium and arsenic salts with hydrogen sulphide in acid solution, but in this case it is difficult to prevent the partial reduction of the arsenic to the trivalent form and the consequent formation of the solid solutions, $xTl_2S.yAs_2S_3$.

On the other hand the solid solutions $xTl_2S.yAs_2S_3$ can be transformed into Tl_3AsS_4, by treament with sodium polysulphide. The compound Tl_3AsS_4, thallium sulpharsenate, is an orange colored precipitate insoluble in dilute alkaline sulphides. On boiling with a concentrated solution of sodium sulphide it is partially decomposed, some arsenic pentasulphide going into solution and thallous sulphide remaining. Dilute acids decompose it with the evolution of hydrogen sulphide, thallium going into solu-

[1] Z. Kryst., 28, 97 (1895).

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tion and arsenic pentasulphide remaining. When washed with water and dried it is perfectly stable in the air at ordinary temperatures, but it melts with slight decomposition at about 250°. This compound may also be used in the gravimetric determination of thallium in a manner similar to the thallium sulphostannate method.

Thallous Sulphide and Antimony Trisulphide; *Thallous Sulphide and Antimony Pentasulphide.* Thallous sulphide forms with both antimony trisulphide and antimony pentasulphide mixed precipitates similar to the solid solution $xTl_2SyAs_2S_3$. The two series of combinations, thallous sulphide with antimony trisulphide and thallous sulphide with antimony pentasulphide, are not readily distinguishable from each other by their physical properties and can be described in nearly the same words. The two entire series of compositions from pure thallous sulphide to pure antimony trisulphide or antimony pentasulphide are homogeneous, showing a complete series of solid solutions in each case. These solid solutions vary in color from black when high in thallous sulphide through red to orange when high in the antimony sulphide. Dilute acids readily dissolve some of the thallous sulphide, the solid solution becoming richer in the antimony sulphides and hence more resistant toward acids, so that only warm concentrated acids will completely remove the thallium sulphide. In the same way dilute alkaline sulphides partially dissolve the antimony suphides but only hot concentrated alkaline sulphides will completely remove the antimony sulphides. These solid solutions are stable in the air except when high in thallous sulphide; then they are readily oxidized especially when not completely dry. Most of these solid solutions of intermediate composition if heated to about 100° in the air or even in the solution in which they are prepared sinter and become black and vitreous without change in composition.

Thallous Sulphide and Stannous Sulphide. Thallous sulphide and stannous sulphide form a complete series of solid solutions when precipitated together in acid or alkaline solutions. By starting with a solid phase high in thallous sulphide and gradually dissolving out the thallous sulphide with dilute sulphuric acid the whole series of compositions was obtained. Different compositions were also obtained by precipitating mixtures of stannous and thallous salts with colorless sodium sulphide. The precipitates obtained by either of these methods were found on microscopic examination to be entirely homogeneous. The color varied from black when rich in thallous sulphide through a light brown to a brownish black when high in stannous sulphide. Dilute acids extract part of the thallous sulphide, the solid becoming richer in stannous sulphide, and more resistant towards acids. Alkaline monosulphides are without

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effect, but alkaline polysulphides change these solutions to thallium sulphostannate.

The Preparation of the Above Substances in Solutions Unsaturated with Hydrogen Sulphide. When any of the combinations of thallous sulphide mentioned in the preceding pages are prepared in solutions unsaturated with hydrogen sulphide, as, for instance, in ordinary sodium sulphide solutions, the solid cannot be filtered and washed without decomposition. This fact was mentioned by Gunning[1] in connection with the thallous-arsenious sulphide combinations when precipitated in alkaline solutions but he did not mention that if the alkaline solution is saturated with hydrogen sulphide the precipitate so prepared is stable on filtering and washing. The difference in the precipitates prepared in solutions saturated or unsaturated with hydrogen sulphide seems to be in the physical state only; the same compounds and the same solid solutions are formed and under the microscope the only difference is that the preparations in solutions saturated with hydrogen sulphide have a greater tendency toward crystalline structure and are not so finely divided. When once prepared in stable form the precipitates can be washed with ordinary sodium sulphide solution for some time without decomposition but finally the washings become turbid; such precipitates can however be washed with water for a very long time without any signs of decomposition. This is of especial importance in connection with the use of thallium sulphostannate in the gravimetric determination of thallium and shows the necessity of employing primary sodium sulphide in the precipitation.

Thallous Sulphide and Sulphur. Carstanjen[2] in his investigations on the compounds of thallium and sulphur obtained two compounds, Tl_2S and Tl_2S_3, which he considered to be well characterized chemical individuals and a series of intermediate products which he described as homogeneous, crystalline substances of similar appearance. Although he expressly stated that these intermediate products might be of any composition between Tl_2S and Tl_2S_3 yet he gave two formulas, $3Tl_2S_3.5Tl_2S$ and $Tl_2S.Tl_2S_3$, which correspond to some of the analyses made and these formulas are given in the literature as representing definite compound Tl_2S with Tl_2S_3. Schneider[3] has also mentioned a compound $Tl_2S.2Tl_2S_3$ which he obtained while endeavoring to prepare a double sulphide of sodium and thallium by melting together thallium sulphate, sodium carbonate and sulphur and extracting the fused mass with water. The composition of this substance also will probably vary with the conditions of preparation. Strecker[4] precipitated an am-

[1] loc. cit.
[2] J. pr. Chem., 102, 76 (1867).
[3] Pogg. Ann., 151, 437; 153, 588 (1875).
[4] Ann. chim. phys., 13, 1255 (1865).

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moniacal solution of a thallic salt with hydrogen sulphide and obtained a brown precipitate which he considered to be Tl_2S_3, but no analyses were made. Carstanjen[1] could obtain a product of the constant composition Tl_2S_3 only by melting thallium with a large excess of sulphur and distilling the excess of sulphur without access of air. Boettger[2] claimed to have prepared a still higher sulphide of thallium as a red precipitate insoluble in dilute acids by boiling a slightly acid thallium solution with excess of sodium thiosulphate. But Gunning[3] showed that such a precipitate was formed in this manner only in the presence of arsenic, although he mentions that an instable red precipitate is formed by passing hydrogen sulphide into a solution of thallium which has been oxidized by aqua regia. Hofmann and Höchtlen[4] prepared a higher sulphide of thallium by dropping thallous chloride into a 25 per cent. ammonium sulphide solution which had been saturated with sulphur. A heavy greenish precipitate was formed which on standing in the presence of the solution slowly became crystalline. These crystals were described as homogeneous, black, shining and opaque. Analyses gave Tl, 72.52 per cent., and S, 29.14 per cent. (calculated for Tl_2S_5; Tl, 71.83 per cent., S, 28.17 per cent.) and the substance was called the thallous salt of hydrogen pentasulphide. The papers cited above comprise the most important observations which have been published on the combinations of thallium and sulphur. The results obtained and the opinions expressed show the need of a systematic investigation of the whole field.

By means of two simple wet processes the whole range of concentrations between thallous sulphide on one end and pure sulphur on the other can be obtained. (1) By treating thallous sulphide with sodium sulphide solutions in which varying amounts of sulphur had been dissolved and which were then saturated with hydrogen sulphide combinations of thallium and sulphur containing from 90.49 per cent. Tl($=Tl_2S$) to about 70 per cent. Tl were obtained. In this method the sodium sulphide solutions must be kept saturated with either sulphur or hydrogen sulphide, otherwise the thallous sulphide will not take up sulphur from the solution. (2) By precipitating an acid solution of any thallium salt with a very slight excess of sodium polysulphide solution precipitates can be obtained which vary in composition from about 25 per cent. sulphur to nearly pure sulphur depending upon the acidity and concentration of the solution of the thallium salt and on the amount of polysulphide sulphur in the sodium polysulphide solution. Microscopic examination of the solids of different compositions obtained by these methods gave the follow-

[1] loc. cit.
[2] Ann. chim. phys., **128**, 248 (1863).
[3] loc. cit.
[4] Ber. **36**, 3090 (1903).

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ing results. Between pure thallium sulphide and about 81 per cent. thallium the solid was entirely homogeneous; from 81 per cent. thallium to 76 per cent. thallium phases were distinguishable, while from 76 per cent. thallium to pure sulphur the solid was again homogeneous. These observations show that under the conditions of formation described above in the system thallium sulphide and sulphur there are two series of solid solutions, one extending from pure thallous sulphide to 81 per cent. thallium, the other from 76 per cent. thallium to pure sulphur. The first of these will be designated the α solid solution, the second one the β solid solution. The α solid solution when formed as above appears dark brown to the eye but when examined under the microscope it is of a light brown color; however, on pressing it firmly between the slide and the cover glass that part which comes in close contact with the cover glass appears entirely black. The general appearance seems to vary in different preparations made as nearly as possible under the same conditions and of the same composition, but, as is most important, the preparations are always homogeneous. When removed from the solution, washed with water and dried the tendency to oxidize and the ease of decomposition with acids decrease as the amount of sulphur increases. The end concentration of the α solid solution where the β solid solution began to appear could be determined only with an accuracy of about 0.3 per cent. thallium, within this limit of error the end concentration is 81 per cent. thallium. From the well defined series of trivalent salts of thallium and from the double sulphides of trivalent thallium with potassium sulphide as described by Schneider[1] and Schneider and Preiss[2] we would expect a definite compound Tl_2S_3. The only safe conclusion to be drawn from these results obtained under one set of conditions is that under these conditions the end concentration of the α solid solutions happens to be near the composition Tl_2S_3. But Carstanjan, as mentioned above, obtained the same end concentration when working under very different conditions, *i. e,* at high temperatures and by dry process, from which it can be seen that the end concentration remains constant under diverse conditions. From all these considerations it may be concluded that the end concentration is 80.93 per cent. thallium ($=Tl_2S_3$) and that Tl_2S and Tl_2S_3 form a complete series of solid solutions. The β solid solution which begins to appear at about 81 per cent. thallium is so strikingly different from the α solid solution that it is very readily distinguished; the α solid solution is amorphous, brown and opaque, while the β solid solution is crystalline, red and translucent. The β crystals are mostly well formed, between crossed Nicols they show parallel extinction and they are apparently orthorhombic. When removed from the solution, washed with

[1] loc. cit.

[2] Pogg. Ann., 138, 604 (1870).

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water and dried they are entirely stable in the air showing no tendency to oxidize. They are much more resistant to the action of dilute acids than is the α solid solution, but alkalies and alkaline sulphides which are not sufficiently saturated with hydrogen sulphide or with sulphur readily decompose them by extracting sulphur. By the first method mentioned above, a solid with as low as 70.3 per cent. thallium can be obtained and for compositions with less thallium the second method must be used. The precipitates obtained by the second method are not well crystallized because their formation is so rapid, but in their color and other properties they resemble the more crystalline precipitates obtained by the other method. As the amount of thallium decreases the color becomes lighter and more of an orange tint, finally fading to the yellow of pure sulphur, while their stability in the presence of acids increases. When boiled with dilute acids the β solid solution gives up thallium sulphide, becoming richer in sulphur until finally the acid has no further effect. The only acid which will completely extract the thallium sulphide is fuming nitric acid and this acts only in consequence of its ability to oxidize some of the sulphur. Although thallous sulphide is practically insoluble in ordinary colorless alkaline sulphide solutions yet as more sulphur is dissolved in the solution and as more sulphur is in the solid in equilibrium with the solution the solid becomes more soluble until in solutions saturated with sulphur an appreciable amount of thallium can be found. On pouring slowly a dilute solution of any thallium salt into a warm solution of an alkaline sulphide saturated with sulphur at first a yellow precipitate forms but this dissolves on shaking. If as much thallium as will dissolve is added and the solution is allowed to cool, yellowish red crystals of the β solid solution separate out. These crystals contained not a trace of the alkalies used and there seems to be no tendency toward the formation of the double sulphides which were prepared in the dry way by Schneider[1]. It is difficult to see why with the same general method of preparation Hofmann and Höchtlen obtained crystals which were black and opaque instead of red and translucent. If the thallium solution is added too rapidly and the precipitate is not given opportunity to reach equilibrium with the solution, part of the precipitate will appear black and opaque under the microscope, but on crushing these black lumps between the cover glass and the slide the smaller particles will transmit red light. By having an excess of alkaline polysulphide present and by allowing the mixture to stand in a warm place for several days with frequent shaking the whole solid can be obtained in well formed crystals which are red and translucent. The constancy of the composition of the sulphide obtained by Hofmann and Höchtlen was

[1] loc. cit.

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due to the constant concentration of the sulphur in the ammonium polysulphide solutions used.

CORNELL UNIVERSITY,
April, 1907.

THE VANADIUM SULPHIDE, PATRONITE, AND ITS MINERAL ASSOCIATES FROM MINASRAGRA, PERU.

BY W. F. HILLEBRAND.

Received May 23, 1907.

In the Engineering and Mining Journal, Sept. 1, 1906, p. 385, and in Informaciones y Memorias of the Society of Engineers of Lima, Peru, Vol. 8, pp. 171-185, 1906, are two accounts, by Foster Hewett and José J. Bravo, respectively, of a remarkable vanadium occurrence at Minasragra, about 46 kilometers from Cerro de Pasco in Peru, and 43 from the railway. The two accounts agree on all essential points that are common to both, though that of the Peruvian writer is much the more detailed as to the geography and geology of the region. The data immediately following are drawn from the publications referred to, and from additional information furnished by Mr. Hewett.

Cretaceous sedimentaries—shales, sandstones and limestones—dipping at about 45° have been intruded by two (Hewett) or three (Bravo) series of eruptive dykes, and at the point of greatest frequency of these intrusives occurs the vanadiferous deposit, which had as yet been opened up only very superficially by a few pits along an extension of 400 feet on the outcrop. The vanadiferous materials occur in vein formation and are three in kind, aside from alteration products that cover the surrounding surface. Under the hanging wall is a thickness of about eight feet of an amorphous material of complex mineral composition which will be designated hereinafter as the "ore." Its color is dark, almost black (dark green like olivenite, according to Hewett, bright lead gray with metallic luster on fresh surfaces but soon tarnishing, according to Bravo). Adjoining this material, without distinct line of demarkation beneath, is a singular, hard, coke-like carbonaceous matter, from eight inches to two feet in thickness, which blends on the farther side into a lustrous, black substance of from four to six feet thickness, designated as asphaltite by both the above-named writers, although it is a sulphur compound of carbon with very little hydrogen.

These three substances will now be considered in detail, beginning with the last, which, from its unique position among carbonaceous mineral substances, seems worthy of a specific name for the purpose of more ready separation from those bitumens and coals which it so strongly resembles in its superficial aspects. The name *quisqueite* is suggested by Mr. Hewett, after the settlement nearest to the locality of occurrence.

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The materials described in the following pages were furnished by Mr. Hewett, and a portion of the chemical data published by him were based on incomplete preliminary tests by myself. The reason for examining them in detail in the laboratory of the U. S. Geological Survey is not only that they represent an occurrence and association so unique, but chiefly that an as yet undescribed association of vanadium and carbonaceous matter in eastern Utah presents some points of similarity with that of Peru, and by reason of the higher concentration in the latter they seemed to offer a convenient stepping stone to future research upon the North American occurrence.

As to the source of the materials composing this vein deposit, nothing can at present be said, nor is a satisfactory explanation at hand for the comparatively sharp separation, in what would seem to be one vein, of such unlike materials. Mr. Hewett remarks that "the appearance of the materials as well as their occurrence strongly suggests that they were forced into the shales in a plastic or even liquid condition. Subsequent metamorphism has altered the composition of the asphaltite and the condition of the sulphur in the sulphide material." It is conceivable that the injected material was originally homogeneous and that segregation took place after injection. Possible evidence in favor of this view is afforded by the fact that the rich vanadiferous ore contains several per cent. of carbonaceous matter similar in composition to the quisqueite, that the carbonaceous matter is itself vanadiferous, and that both are extremely rich in sulphur. In order to account for the coked matter between the two, it would seemingly be necessary to assume that the requisite heat came from the side of the vanadium sulphide ore. The adjacent dyke undoubtedly played the chief rôle in this connection.

This is not the only known association of vanadium with carbonaceous matter, an association which is undoubtedly significant though we are as yet unable to explain it. Aside from the above-mentioned occurrence in Utah, vanadium has been reported in numerous coals, in grahamite that probably came from West Virginia, and Mr. Hewett tells me that it is a constituent of the grahamite from Oklahoma. The enormously high proportion of vanadium in the Peruvian occurrence is of special interest not only on that account but because it offers an opportunity to determine its state of combination in at least this particular case. It is possible that in some instances such sources may have furnished the vanadium of deposits of secondary minerals like those of the western United States.

Quisqueite.—This material, the asphaltite of Hewett and Bravo, though rich in carbon is worthless as a combustible, because of its content in sulphur which exceeds that of the carbon in the specimen examined. Mr. Hewett reports 45 per cent. of sulphur, and that, though

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not holding a flame, the material burns when heated with the blue flame of sulphur. It is brittle, with density 1.75, and hardness about 2.5. It is infusible, and apparently not affected by the usual solvents for bitumen, except that carbon disulphide extracts much sulphur. It leaves a variable amount of highly vanadiferous ash — 3.31 per cent. containing 0.544 V_2O_5 (Hewett), 0.80 per cent. likewise high in vanadium (Hillebrand). Much sulphur sublimes when the mineral is heated in a closed tube, and later hydrogen sulphide is evolved. It is oxidized by long boiling with strong nitric acid. The following is the composition of the sample analyzed :

S soluble in CS_2	15.44
S combined	31.17
C	42.81
H	0.91
N	0.47
O by diff.	5.39
Moisture at 105°	3.01
Ash	0.80
	100.00

The ash afforded roughly : SiO_2, 0.04 ; Al_2O_3, 0.08 ; Fe_2O_3, 0.10 ; NiO, 0.06 ; V_2O_5, 0.52. These are, however, results of minor quantitative value, because of the minute amount analyzed. It is practically certain, for reasons to appear later, that the vanadium, iron and nickel existed in the original material as sulphides, and, therefore, assuming that the main analysis is correct, that the oxygen reported is too low.

The composition of this material is, so far as my knowledge extends, unique, and there are no data known that throw light on its chemical structure.

The Coke-Like Material.—The quisqueite seems to have been converted on its upper side into a sort of coke, though this differs markedly from artificial cokes. Its hardness is 4.5. Glancing blows of a hammer cause much sparking. It is somewhat vesicular, though without large cavities. The openings are mostly short, thin contraction cracks without orientation, which are best observed under a lens. They are for the most part lined or filled with a thin, brilliant, pitchy black coating, often reticulated, of what appears to have been originally fused matter, and to which the luster of much of the specimen, when freshly broken open, is due. There are also rather numerous minute blowholes lined with or sometimes loosely filled with the brittle, pitchy matter just mentioned. Elsewhere the surface is rather dull, and of a color having a suggestion of red when contrasted with the pitch-black of adjacent parts. The texture is extremely fine-grained like that of steel, and the fracture rather conchoidal. These peculiarities of texture often give rise to great unevenness on large fracture surfaces. In the closed tube

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there appears a sublimate of sulphur and then the odor of hydrogen sulphide.

The composition of the sample analyzed follows:

S soluble in CS_2	0.64
S Combined	5.36
C	86.63
H	0.25
N	0.51
O by diff	4.64
Moisture	None.
Ash	1.97
	100.00

The ash is highly vanadiferous.

The Vanadium Ore

The remainder of the deposit, about eight feet in thickness, is a complex mixture of mineral substances. The color in mass, as earlier mentioned, is dark, almost black, with perhaps a suggestion of green as stated by Hewett. It breaks for the greater part unevenly, but often somewhat smoothly along planes of weakness, portions of which show permanent brilliant metallic luster. This is due to a thin coating of presumably carbonaceous matter like that noticed in the coke-like material. Bravo reports enclosures of brilliant black "asphaltite" and also sulphur visible to the naked eye. No sulphur was to be seen in the samples at my disposal,[1] but there were many patches and points of a dull pyritous mineral whiter than pyrite and usually of a faint reddish cast apparently due to tarnish. These consist of an iron-nickel sulphide, of which more anon, carrying vanadium and siliceous and titaniferous matter. Heated in the closed tube the ore gives off sulphur copiously and then hydrogen sulphide. It does not melt.

The chief component was given in both the earlier publications as a vanadium sulphide to which Hewett gave the name *patronite* and Bravo that of *Rizo-Patronita*, in honor of Senor Antenor Rizo-Patron, the discoverer of the ore and its vanadium contents. The paper of Hewett was published Sept. 1, 1906, and that of Bravo bears the date Aug. 31 of the same year, hence must have appeared a little later, although in the August number of the Boletin de la Sociedad de Ingenieros. Hewett's name, therefore, has the right of priority and being shorter is preferable, even though that given by Bravo may better conform to Spanish usage as to derivation, since it embodies the whole patronymic.

The following analyses, given by those authors, show the composition of the ore incompletely, since appreciable percentages of nickel and titanium were overlooked, and, moreover, they also show that it varies

[1] Specimens received from Mr. Hewett since the above was written do show sulphur as scales in parting surfaces.

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much in respect to the relative amounts of siliceous and sulphide components.

	Analysis by J. O. Handy, (Pittsburg).	Analysis by H Bunting, (Lima).
SiO_2	10.88	22.22
Al_2O_3	3.85	8.32
Fe	2.45	1.98
V	16.08	15.36
MoO_3	0.50	——
S soluble in CS_2	6.55	{ 41.81
S combined	54.06	
CaO	——	0.33
Moisture	Trace.	——
Undetermined	[5.63][1]	9.98[2]
	[100.00]	100.00

Both I (in Mr. Hewett's paper) and Bravo reported the solubility of the vanadium in fixed caustic alkalies, and Bravo likewise in ammonia. I may say that ammonia does not act so quickly as the fixed alkalies. Bravo analyzed the alkaline extract for sulphur and vanadium, after first removing free sulphur, and reported 32.89 per cent. vanadium and 67.20 per cent. sulphur, corresponding approximately to the formula VS_3 (the ratio as calculated by me from his values is 1:3.28).

The complete analysis of this ore is extremely difficult, and in some respects the results given on p. 1025 are lacking in precision. The following behavior threw light on the nature of the mineral components:

Repeated treatment in a Soxhlet extractor with carbon disulphide removed considerable sulphur. After thorough drying of the capsule and contents, hot water was passed through. The aqueous filtrate was blue-green and held a sulphate or sulphates of vanadium. This operation was followed by extraction with warm caustic soda as long as the filtrate came through colored. Hereby nothing but vanadium, sulphur and some of the siliceous components were taken out, and the solution was of a cherry red color. In it the proportions of vanadium and sulphur were determined.

It may be said here that the analysis was of necessity made with interruptions, and it was noticed that the values obtained for free sulphur increased with lapse of time. The first determination gave 4.5 per cent., the second 5.5 per cent., and the third 7 per cent. sulphur, each on a separate portion of the same sample. This seemed to indicate a progressive oxidation of the vanadium sulphide with liberation of free sulphur, or else that the ore contained insoluble as well as soluble sulphur, and that the former on exposure of the powder to air underwent rather rapid conversion to the soluble modification. Heating the powder for

[1] Largely carbonaceous.

[2] Carbon.

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some hours with a little carbon disulphide in a sealed tube in a steam bath did not result in an increased yield of free sulphur, nor did heating the powder to 60° for some hours in air do so; hence the latter explanation seems improbable. To test the former the portion of powder that had afforded 7 per cent. sulphur and had then been extracted by hot water was allowed to dry thoroughly and left exposed to air under an inverted beaker for three weeks, after which time it was again tested for free sulphur and sulphate, both of which were found, thus apparently confirming the supposition of oxidation. But the free sulphur found in this test was so far in excess of that converted to sulphate that it would seem as if the liberation of sulphur took place much faster than the oxidation of that which remained in combination with the vanadium (see p. 1025).

It was impracticable satisfactorily to examine the material remaining in the Soxhlet capsule after extraction by carbon disulphide and water, but separate portions of the ore, treated directly with alkali, were used in part. From the residue thus obtained strong nitric acid after a few minutes' action took out all the iron-nickel sulphide together with most of the remaining vanadium, all the molybdenum and some titanic oxide, silica and alumina, besides acting to a slight degree, perhaps, on the carbonaceous component of the ore. The sulphur of the metallic sulphide was apparently wholly oxidized by the nitric acid. The solution was analyzed, but for more exact determination of the composition of the sulphide large amounts of the ore, only coarsely broken up, were thoroughly extracted by alkali, the black residue was dried and rubbed down gently with the finger, and from it the sulphide was extracted by an electromagnet and purified by repetition of the treatment.

The residue not dissolved by nitric acid is black, and contains most of the carbonaceous matter of the ore besides the titaniferous and siliceous matters not removed by the foregoing operations. The carbonaceous material contains much sulphur and seems in this respect to resemble the quisqueite already described. On burning it off there is left a straw-colored residue in which nothing mineralogically definite was recognized except a few quartz grains. It is not unlikely that it consists chiefly of a clay-like substance and titanium dioxide in an amorphous state. Some vanadium in an oxidized form, perhaps a constituent of the clay, is also present.

It thus appears that the sulphur and vanadium exist in four different forms in the powdered ore. Mr. Hewett states that lead, zinc, copper, arsenic, antimony, calcium, magnesium, silver, gold and platinum were sought but not found. Uranium and germanium were looked for in vain by myself. Prof. B. B. Boltwood, who kindly examined for me both

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the vanadium ore and the quisqueite, reports hardly any evidence of radioactivity.

Bulk Analysis of the Ore.—The results in the following analysis are not in all cases highly accurate, and the summation is affected by indeterminable errors among which is too high water, because some of it is derived from the hydrogen of the carbonaceous matter. This error is to a large extent offset by the oxygen of the carbonaceous matter. The vanadium sulphide constitutes about two-thirds of the ore, the metallic sulphide over one-tenth. It is not only an ore very rich in vanadium, and from which the latter can be very readily extracted, but it also carries a percentage of nickel that may prove commercially of much value, since it will be left wholly in the residues after extraction of the vanadium.[1]

S (total)	58.79 (4.5 free).
V "	19.53
Mo	0.18
Fe	2.92
Ni	1.87
C	3.47
SiO_2	6.88
TiO_2	1.53
Al_2O_3 (P_2O_5)	2.00
Fe_2O_3	0.20
MnO	trace
Cr	trace?
Alkalies	0.10?
H_2O	1.90
O from V. sulphate	0.38
	99.75

Free Sulphur and Water-Soluble Extract.—Several determinations of the sulphur extractable by carbon disulphide were made at considerable intervals of time. The first gave 4.5 per cent., the second 5.5, and the third 7 per cent., thus, as already said, indicating a progressive liberation of free sulphur. The extractions were made in a Soxhlet apparatus till an extract was found free from sulphur.

The first determination of the water-soluble extract gave 0.41 per cent. SO_4 and the solution held vanadium, as shown by its blue-green color and by qualitative test. Much later, in another portion, there was found 1.23 per cent. SO_4 and 0.92 per cent. V, with ratio V to SO_4 of 1 to 0.71. The vanadium was in an intermediate stage of oxidation between V_2O_4 and V_2O_5, as ascertained by direct titration and again after reduction by sulphurous acid.

When the powder that had served for the last test, and which had

[1] On specimens received from Mr. Hewett since the above was written there is either none of this sulphide visible to the eye or only a few small particles.

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afforded 7 per cent. free sulphur, was allowed to dry and left exposed to the air for three weeks and then again extracted by carbon disulphide and hot water in turn, there was found additional 0.81 per cent. of SO_4 and 0.40 per cent. of V, but the vanadium of the aqueous extract was all in the V_2O_4 state, for after titrating directly and then again after reduction by sulphurous acid, the results were identical. The ratio of V to SO_4 was not, however, the same as in the previous test, being 1 to 1.07. In this last test there was found 3.83 per cent. of free sulphur in addition to the 7 per cent. found at first, and since the sulphur in the SO_4 is but 0.27 per cent., or but one-fourteenth of the free sulphur formed during the three weeks, the ground will be apparent for the earlier remark (p. 1023) concerning the greater rapidity of splitting off of free sulphur from the original sulphide than of oxidation of the lower combination of vanadium and sulphur that presumably resulted from this division. But the variation in the two ratios given above between vanadium and SO_4 has not been cleared up. These approximate very roughly to 1 to 1, which indicates a similar ratio in the lower sulphide to whose direct oxidation the sulphate is supposed to have been due, that is VS. But much more knowledge is needed, based on numerous and varied tests, before the reactions involved in the changes above indicated can be written.

Patronite.—Several determinations of the sulphur and vanadium in the alkaline extract, after first removing free sulphur and the water-soluble constituents, gave the following results :

V	19.16	18.89	19.09	18.46
S	47.74	47.84	45.65	44.74
Ratio.....V : S	1 : 3.97	1 : 4.04	1 : 3.82	1 : 3.87

The determinations with the highest two ratios were earlier analyses in which least free sulphur was found, and presumably least oxidation had taken place. They point to a formula VS_4 for the sulphide instead of VS_3 as reported by Bravo whose actual ratio was 3.28. A sulphide of this composition seems very singular, and the possibility suggested itself that the compound might be ortho-sulphovanadic acid, but this would probably be soluble in water and an amount equal to that in the ore would need, moreover, above 1 per cent. of hydrogen, whereas the total as represented by the water found is less than 0.20 per cent., and this unquestionably belongs largely with the siliceous and aluminous matter of the ore.

In the light of the observation relating to the splitting off of free sulphur from the sulphide, a process that is evidently connected with exposure to air, the possibility has to be considered that the free sulphur found in the test showing least may all have been originally combined with the vanadium to form a still higher sulphide than VS_4. The ratio

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calculated on this basis is less than 1 to 4.5, indicating a formula not above V_2S_9. Lacking, as we do, any knowledge regarding the higher sulphides of vanadium, speculation at present would be premature.

Whatever may be the true formula the mineral is new, and the name patronite may well be applied to it.

The Iron-Nickel Sulphide, a Highly Nickeliferous Pyrite.—The bulk analysis of the ore indicates a greater percentage of the iron-nickel sulphide than would be supposed by inspection, and than was obtained by separation in the manner already outlined. Much of it is evidently in a state of fine division, and escapes in the washings. Indeed, it was sought to recover only the grains of some size. It was noticed after separation that while some of the larger grains especially showed the pyritous color on fracture surfaces, all were more or less covered with a black coating of what is assumed to be the carbonaceous material of the ore, and that most of them were black throughout, apparently from the same cause, since on solution in nitric acid a considerable carbonaceous residue was left. In a few instances apparent crystals, seemingly of octahedral habit, were observed, but otherwise the fragments were quite destitute of crystalline structure. The color is rather whiter than that of pyrite, as said before, becoming of a reddish cast by tarnish. The mineral is not attracted by a hand magnet but attaches itself readily to an electromagnet. The density of the material analyzed was 4.33, but this value is of little worth, since despite repeated purification the fragments contained a good deal of carbonaceous, siliceous and titaniferous matter in a state quite invisible to the eye. Heated in a closed tube much sulphur is evolved. The mineral is very insoluble in hydrochloric acid, but is readily attacked by nitric acid with complete oxidation of the iron, nickel and sulphur. The other constituents remain more or less unattacked according to the duration of contact with the acid.

The results given below are for the four chief constituents the mean of concordant determinations. It is to be noted that if the vanadium was counted as the element every analysis gave a summation of approximately only 97 per cent. This is accounted for in part, probably, by the extreme oxidizability of the mineral when exposed in powder form to the air, especially when wet. Hot water extracts from the powder ferrous and nickelous sulphates with only a very little vanadium. If the powder is left moist on the filter, relatively large additional quantities of iron and nickel can be extracted next day, and for several successive days, with very little vanadium. But the discrepancy cannot be apparently in large part thus accounted for. It seems necessary to assume that the vanadium is in an oxidized form, perhaps as a constituent of the siliceous-aluminous material. In this case its condition would be that of trivalency in all probability, a condition which also affords a

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more satisfactory summation than that of quinquivalency. Against its presence in combination with silica and alumina is its great excess over that in which it is known to occur in such forms in nature. On the other hand the matter insoluble in nitric acid still contains some vanadium.

The following experiment seems to put it beyond question that the vanadium is not a constituent of the metallic sulphide. When the powder was exposed over night in a covered platinum crucible to the action of strong hydrofluoric acid, nearly half the vanadium and much of the silica, alumina and titanium, were extracted, but only about one-twenty-fifth of the iron and nickel, these two showing exactly the ratio afforded by the main analysis below. Boiling with dilute sulphuric acid yielded results somewhat similar.

	Mean		Atom. Ratio			Calc. to 100
S	45.06[1]	÷32.06	=1.455		=2.02	52.31
Fe	25.38	÷55. 9	=0.454	0.721	=1.00	29.46
Ni	15.70	÷58. 7	=0.267			18.23
Co	Trace					—.—
V	4.31	= 6.33 V_2O_3 or 7.66 V_2O_5				100.00
Mo	0.09					
C	0.47					
H_2O	1.38	(partly from H of carbonaceous matter).				
TiO_2	0.93					
SiO_2	1.93					
Al_2O_3	2.45	(with a little P_2O_5)				
	97.70					

If the vanadium is disregarded, the iron-nickel sulphide has the formula $(FeNi)S_2$ with iron to nickel as 1.70 to 1, or nearly 5 to 3. A pyrite with such a high proportion of nickel is unknown. But a single one of the analyses quoted in Hintze's Handbook of Mineralogy shows anywhere near 6 per cent. nickel; this one, however, showing also about 3 per cent. of cobalt. The nearest approach to the present case is seen in the mineral gunnarite, $3FeS_2$, $2NiS$, incompletely described by Landstrom[2] with density 4.3 and a tin-white color with a tinge of yellow, tarnishing yellowish-brown. The present mineral would seem to be quite distinct from gunnarite, and for the present is to be regarded as a highly nickeliferous pyrite. Should it seem proper to give it a specific name later, *bravoite* is suggested, after Señor José J. Bravo, the Peruvian writer on the vanadium occurrence at Minasragra.

The Carbonaceous Material of the Ore.—A determination of the carbon and sulphur in 0.2459 gram of the residue insoluble in alkali and nitric

[1] This does not include the sulphur that may have been held by the undissolved carbonaceous matter.

[2] Geol. Fören., 9, 368, 1887.

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acid gave 0.0475 carbon and 0.0254 sulphur, of which last 0.0036 was soluble in carbon disulphide. These figures indicate a similarity to quisqueite, although the sulphur is lower.

The Oxidation Products of the Ore.—These are reported to cover the surface of the ground in the vicinity of the vein outcrop. The specimen examined by me resembles porous limonite in appearance. There was found in it by a rough partial analysis about 45 V_2O_5, 14-15 Fe_2O_3, 15 H_2O, 20 or more of siliceous gangue, nearly 1 of MoO_3 and a little SO_3. Nickel is absent, or practically so. The material does not represent a single species, for it contains probably more than one vanadium compound, among them doubtless the minute micaceous scales, greenish sometimes, and sometimes yellowish, that may be seen with a lens.

LAB. U. S. GEOLOGICAL SURVEY,
May 22, 1907.

THE NITROSO-β-NAPHTHOL METHOD FOR THE QUALITATIVE SEPARATION OF NICKEL AND COBALT.

BY WILLIAM H. CHAPIN.

The Nitroso-β-naphthol method for the qualitative separation of nickel and cobalt is not a new one; and, in view of what has already been written on the subject, anything further may seem superfluous. However, this paper has two excuses to offer for its existence:

First—For the sake of those who are unacquainted with the method, it will aim to make the directions for the cobalt test more explicit than those usually given.

Second—It will present a method for determination of the nickel, which so far as the author knows is new.

The things this paper contains may be familiar to many; but for the sake of benefitting those who are still wandering in the dark, I shall brave the fear of repetition, and give them out for what they are worth.

Cobalt. Beginning at the point where the nickel and cobalt exist alone as sulphides after removal of zinc and manganese, we proceed as follows:—

Place paper and contents in a casserole, add 10 cc. dilute hydrochloric acid (1:4) and 1 cc. dilute nitric acid (1:3) and boil until only the paper and separated sulphur remain undissolved. Now filter, washing the paper slightly, return the filtrate to the casserole, and boil down to complete dryness, taking care to remove the casserole from the flame a little before this point is reached, so as not to overheat and render the residue insoluble. Take up with two or three drops of dilute hydrochloric acid and 10 cc. hot water, and add a solution of nitroso-β-naphthol in slight excess. The cobalt comes down as a very bulky brick-red precipitate of cobalti-nitroso-β-naphthol, $Co(C_{10}H_6ONO)_3$. After stirring and allowing to stand a few minutes, filter, and confirm the presence of cobalt by means of the borax bead. Before testing for nickel, add a

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few drops more nitroso-β-naphthol to the filtrate to make sure that the cobalt is all removed, and of course filter off any precipitate that may be formed.

NOTES.—Hydrochloric acid in large quantities and nitric acid even in small quantities interfere with the precipitation of cobalt; hence the evaporation.

The solution of nitroso-β-naphthol is made up as follows:—Weigh out 8 grams of the solid reagent, dissolve in 300 cc. cold glacial acetic acid, dilute with an equal volume of water, and filter. In this way is obtained a saturated solution in 50% acetic acid. For best results, the reagent should be made up as often as once a month, as it does not keep very well.

Owing to the bulkiness of the cobalt precipitate, we usually make up our unknowns with only a small amount of cobalt present (2 gm, crystallized cobalt nitrate per liter). Giving out about 5 cc. of such a solution in an unknown, only about 3 cc. nitroso-β-naphthol solution will be required for complete precipitation. It is, however, by no means necessary to limit the quantity of the cobalt.

The test for cobalt, as above stated, has always given perfectly satisfactory results even with beginners, good tests for cobalt being obtained with certainty, when the quantity present was less than a milligram. Indeed, we have had difficulty in obtaining nickel salts of such purity that our students would not obtain a test for cobalt even when we did not intend it to be present.

Nickel. The main difficulty we have experienced with the method has rested with the test for nickel. In their usual form the directions for this test read as follows: "Make the filtrate from cobalt alkaline with ammonium hydroxide filter off the precipitated nitroso-β-naphthol, and pass hydrogen sulphide. Confirm the presence of nickel by means of the borax bead."

So far as our experience goes, the test in this form has always been a failure. With our classes, failure became so common that the students lost all confidence in the method, and reported largely at random. We even made up our unknowns so that the amount of nickel exceeded that of cobalt ten to one (which only showed the weakness of the method and in no wise overcame it) and even then the number of failures was scarcely less. However, considering the shortness and simplicity of the method and its accuracy for the detection of cobalt, we determined not to give it up without some attempt at making it what it promised to be.

Thinking that possibly the nickel might be lost during the washing of the sulphides, as a result of oxidation and consequent solution, we investigated and found that the loss of nickel from this cause was not

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worse than the loss of cobalt, which amounted to very little.

Next, we tested the solubility of nickel sulphide in the cold dilute (1:10) hydrochloric acid used to dissolve out zinc and manganese, but here again the loss was found to be very small.

At last we turned our attention to the final filtrate in which hydrogen sulphide had failed to give a precipitate of nickel sulphide when nickel salts were known to be present in the original solution. We thought that perhaps the organic matter left in the solution was preventing the precipitation, but were surprised to find that this filtrate contained no nickel. The cause of the difficulty was now plain: In making the solution alkaline, and filtering off the precipitate of nitroso-β-naphthol, we were removing from the solution large quantities of nickel, the amount removed depending upon the excess of nitroso-β-naphthol.

What we needed, then, was a method by which we could remove the nitroso-β-naphthol, so that the solution might be made alkaline for precipitation of nickel without removing the nickel. The method most easily worked out seemed to be the common one for removal of organic matter, viz:— oxidation by means of sulphuric and nitric acids. Trial proved the method to be quick, easy and always successful. Best of all, it did not interfere in any way with the subsequent test for nickel.

The details of this process, as we apply it, and of the final test for nickel are as follows:—

To the filtrate from cobalt add 5 cc. of dilute sulphuric acid (1:5) and 1 cc. of nitric acid (1:3), and boil down in a casserole until dense white fumes of sulphur trioxide are evolved. If a dark color still remains, cool somewhat, add two or three drops more of nitric acid and again heat until fumes of sulphur trioxide appear. By this time all organic matter should be removed and the solution should be colored only yellow at most. Cool now completely, cautiously add 5 cc. water and a piece of litmus paper, and then drop in ammonium hydroxide with constant stirring until the paper is distinctly blue, but avoiding an excess. Now remove the paper, transfer the solution to a test tube, and pass hydrogen sulphide. A black precipitate is probably nickel. Confirm by means of the borax bead.

NOTE.—If through careless work the cobalt is not all removed in its proper place, the excess will appear with the nickel; or, if no nickel is present, in place of the nickel. However, we have never seen enough cobalt carried over to obscure the bead test for nickel, where that element was present; and, on the other hand, in absence of nickel, the bead test never fails to disclose the identity of the small amount of cobalt sometimes carried over. If the work is carefully done, no cobalt will ever be carried over, as its removal by this process is quantitative.

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We have been using this method for the nickel determination long enough to discover the weak points, if there were any, and are perfectly satisfied with the results. Failure on the part of our students is a very rare thing, although we have greatly cut down the amount of nickel in our unknowns. I think we are safe in saying that the test for nickel is fully as delicate as that for cobalt; and the ease and rapidity with which it is carried out make it the best method, in our estimation, we have ever used.

ON PRECIPITATED SULPHUR.[1]

By R. H. Brownlee.

Received May 20, 1907.

Historical.—Ever since, in the year of 1848, Deville[2] first discovered amorphous sulphur and Selmi[3] found the same substance in flowers of sulphur, many chemists have studied its occurrence and its properties. St. Claire Deville[4] examined numerous specimens of commercial flowers of sulphur and found that the percentage of the insoluble amorphous modification varied from 11.3-23.4 per cent. In roll sulphur he found 2.9 7.3 per cent. of sulphur insoluble in carbon disulphide. Deville[5] was the first to notice that the sudden cooling of melted sulphur gave sulphur insoluble in carbon disulphide. After sudden cooling of sulphur from 230° Berthelot's[6] method of measurement[7] gave 60 per cent. of the amorphous variety. After pouring the hot sulphur into ether his method of extraction gave 70 percent. After heating the sulphur with a small quantity of iodine and cooling suddenly in water, the method used seemed to indicate the presence of as much as 80 per cent. of amorphous sulphur.[8]

Berthelot[9] also prepared amorphous sulphur by precipitation from various compounds of sulphur by means of acids and other reagents. He says[10] "In general the kind of sulphur disengaged is independent of the agent used for precipitating, provided it is not an alkali or an oxidizing

[1] The work upon this paper was carried on simultaneously with that published by Smith, Holmes and Hall, Journal of the American Chemical Society, 27, 797, 979, and was read in abstract by Alexander Smith on June 30, 1906, at Ithaca, N. Y., before the American Chemical Society.

[2] Pharm. Centrh., 1848, 200; Graham Otto's "Lehrbuch," 1, 538.

[3] Graham Otto's "Lehrbuch," 1, 539.

[4] Graham Otto's "Lehrbuch," 1, 539

[5] Compt. rend., 26, 119; Ostwald's "Lehrbuch," 2, 2, 551.

[6] J. pr. Chem., 71, 360.

[7] In the experiments referred to, Berthelot did not allow the precipitated sulphur to harden, but extracted the viscous mass with carbon disulphide immediately. It is evident that much of the sulphur could not come in contact with the solvent, and hence a high percentage of amorphous sulphur would be indicated.

[8] Compt. rend., 56, 39.

[9] Ann. (3) 49, 430.

[10] loc. cit. p. 444.

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agent, and that its activities are exercised rapidly without notable heat formation."

He concluded that the state of combination of the amorphous sulphur in the original compound alone regulated the proportion of amorphous sulphur, and that negative sulphur is precipitated completely soluble, and positive sulphur completely insoluble in carbon disulphide. For instance a sulphide should invariably give soluble sulphur and sulphur dioxide insoluble amorphous sulphur. In the same paper, however, he states that the amounts of amorphous sulphur obtained from a given amount of sodium thiosulphate when treated with acids varies with the conditions. Weber[1] observed that by treating potassium polysulphides with very dilute nitric acid he obtained sulphur of which only 86 percent was soluble in carbon disulphide, thus not confirming the observations of Berthelot.

It has been possible to substantiate the observations of Weber, and further to show that the kind of sulphur disengaged from a given compound is not independent of the precipitant. Cloez[2] thought that sulphur was precipitated from solutions in soluble or insoluble form, according to whether it separates from alkaline or acid solution. While many researches have been carried out upon sulphur, the statements with reference to precipitated sulphur seem to be conflicting, and no one, up to this time, has studied the precipitation of sulphur under definite conditions.

Then, too, the work of Alexander Smith and his collaborators[3], has elucidated the relations of the two forms of liquid sulphur, the yellow mobile S_λ (rhombic sulphur) and the brown viscous S_μ insoluble in carbon disulphide (so-called amorphous sulphur), and has therefore prepared the way for a more exact and instructive study of precipitated sulphur. The formation of S_μ by percipitation in various reactions at or below the ordinary temperature, and therefore in a metastable condition, is a subject of especial interest in the light of the above mentioned conclusions.

Accordingly at the suggestion and under the direction of Professor Alexander Smith of the University of Chicago, I undertook the study of precipitated sulphur with the purpose of investigating the relation between the proportion of amorphous sulphur (S_μ) found in a given sample of precipitated sulphur and the conditions under which the precipitation and hardening of the sulphur took place. In connection with this, it was hoped that an improvement could be made in the formulation of the facts attempted in the rules of Berthelot and Cloez.

In order to obtain a general knowledge of the various actions in which

[1] Watts Dict. of Chem., old edition.

[2] Dammer, 4, 207.

[3] This Journal, 797.

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sulphur is precipitated and to ascertain which conditions influence the proportion of insoluble sulphur and to what extent they influence it, an extensive series of preliminary experiments was made. In Section I a selection of these is given. In Section II the final experimental method is described. In the two following sections, the results in the reactions subjected to exact study are detailed, viz. Section III, the interaction of bromine and iodine, with sulphides and polysulphides; Section IV, the interaction of acids with sodium thiosulphate.

Finally, in Section V, the particular conditions which determine the production and proportion of amorphous sulphur (S_μ) are discussed.

General Features of the Precipitation. To understand what follows, the general phenomena presented by most of the precipitations must be noted. When the reagents are mixed, a very pale, almost white cloudiness appears in the liquid, either immediately, or, when dilute solutions are used, after a brief interval. The cloud is almost always composed at first of fluid droplets, whether the product is ultimately found to contain insoluble sulphur or not. The emulsion settles, and, after the lapse of several hours, or days, the precipitate becomes hard and brittle.

In some instances, the hardening takes place without any change in the form of the material, in other instances, notably when the action has taken place in less concentrated solutions, the droplets flow together forming an oily liquid, and when considerable percentages of insoluble sulphur are produced, the droplets fuse together giving a viscous mass.

The Methods.—In order to be able to analyze the sulphur according to the method we adopted it was necessary after the precipitation of the sulphur, to allow it to harden, so that it could be obtained in powdered form.

In the case of sulphur precipitated from sulphides, this was attended with no difficulty, but with the sulphur precipitated from sodium thiosulphate by acids or by the interaction of sulphur dioxide and hydrogen sulphide, the case was different. Usually the sulphur was precipitated as minute droplets which soon united to form a very viscous mass that in some cases required more than a week before becoming hardened, and in the meantime it was rapidly oxidized by air. To avoid this difficulty, the sulphur was rapidly freed from most of the moisture by pressing between folds of filter paper, or by spreading upon a dry plate. This viscous or sticky and damp product was then ground in a mortar with acetone (a substance miscible with water) and carbon disulphide, and the mixture was allowed to evaporate to dryness. In this way a hard material could be obtained in a fraction of the time usually required in the absence of this special treatment. In order to facilitate the removal of the vapors of the liquid, and at the same time to exclude the air, the filter paper or dry plates on which the material had again been spread were placed over sul-

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phuric acid in a dessicator through which a stream of dry carbon dioxide flowed continuously.

In order to study the problem it was, of course, necessary to determine the percentage of amorphous sulphur formed, in each case, and the method employed was that improved by Smith and Holmes[1]. This method consists in (1) grinding the hardened sulphur in a mortar, (2) sifting through a fine sieve and (3) extracting with carbon disulphide.

Owing to the fact that in some of the experiments it was difficult to prepare any considerable quantity of precipitated sulphur, it was decided to employ five grams for each extraction, (instead of ten,) as used by Smith and Holmes[2].

To test the accuracy of the method when five gram quantities were employed, sulphur containing the amorphous variety was precipitated. After the plastic sulphur hardened it was ground in a mortar, sifted through a fine sieve and extracted. In each case the carbon disulphide overflowed the extraction apparatus five times. That the method was capable of giving concordant results is shown by the following data:

Experiment	Per cent. Amorphous Sulphur
1	23.58
2	23.55
3	23.70
4	23.45

Sources of Possible Error.—There seem to be two sources of possible error in this method. First, (a) the solubility of amorphous sulphur in carbon disulphide, and second, (b) possibility of diminution of the proportion of amorphous sulphur during or after solidification.

(a) *Correction for Solubility of Amorphous Sulphur.*—The first possibility of difficulty, the solubility of amorphous sulphur in carbon disulphide, under the conditions of these experiments, could be disposed of only by proper correction. The amorphous sulphur required for the purpose was prepared by precipitating sulphur from sodium thio-sulphate by means of concentrated hydrochloric acid, and submitting this product after hardening, to a treatment in which extraction with carbon disulphide, pulverization and sifting through a fine sieve were repeated several times, in order that entire removal of the soluble variety might be assured. The entirely soluble precipitated sulphur necessary was prepared by the precipitation of sulphur from calcium polysulphide, by means of dilute hydrochloric acid. Then a series of mixtures was prepared by mixing intimately various proportions of the two kinds of sulphur.

The solubility was determined under the same conditions to which the material was exposed in the main experiments. In each case five grams

[1] Z. physik. Chem., 42, 469.

[2] loc. cit.

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of the sulphur to be extracted was weighed into a thimble made from filter paper that previously had been extracted with carbon disulphide. The thimble was placed in a Soxhlet extraction apparatus and the carbon disulphide allowed to overflow five times.

In the following table the first column gives the percentage of amorphous sulphur originally introduced, the second the quantity of amorphous sulphur left after extraction of five grams of the mixture, with five fillings of carbon disulphide and the third the percentage of amorphous sulphur which had been dissolved.

Per cent. of amorphous sulphur in the mixture	Weight of amorphous sulphur left from five grams	Per cent. of amorphous sulphur dissolved, calculated on basis of total sulphur
10	0.492	0.16
20	0.985	0.30
40	1.970	0.60
50	2.462	0.75
80	3.940	1.20
100	4.925	1.50

Inasmuch as the most careful mixing of the ingredients could not give so complete a dissemination of the amorphous sulphur in these artificial mixtures as probably existed in the mixtures produced by precipitation, it is likely that the solubilities appearing in the table are somewhat smaller than those which natural mixtures of the same concentration would have shown. The amounts added by way of correction to the quantities of amorphous sulphur actually found by extraction were therefore probably somewhat too small.

The curve[1] (Fig. 1) puts the data in a form in which they may be used for the correction of observations. The percentages of amorphous sulphur found are laid off along the ordinate and the corresponding percentages of the amorphous sulphur dissolved, (calculated upon the basis of total sulphur) along the abscissa. Thus, the percentage to be added to the percentage of amorphous sulphur found, in each specimen, could be read directly from the curve. These corrections have been applied to all the results given and the final results are expressed in percentages of amorphous sulphur thus shown to be present in the precipitated sulphur.

(b) *Possibility of Diminution of the Proportion of Amorphous Sulphur During and After Solidification.*—In the second place, the percentage of amorphous sulphur (S_μ) might diminish perceptibly during the time which necessarily elapsed between the precipitation and the accomplishment of the hardening of the sulphur.

The question whether the proportion of insoluble sulphur found in the

[1] Smith and Holmes, Z. physik. Chem., 42, 469, plotted the weight of amorphous sulphur left in ten grams of the mixture against the weight of amorphous sulphur dissolved.

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final product of hardening represented the amount actually formed by the interaction and present in the plastic material when first precipitated is discussed in Section V. That the loss of S_μ, by reversion after solidification,

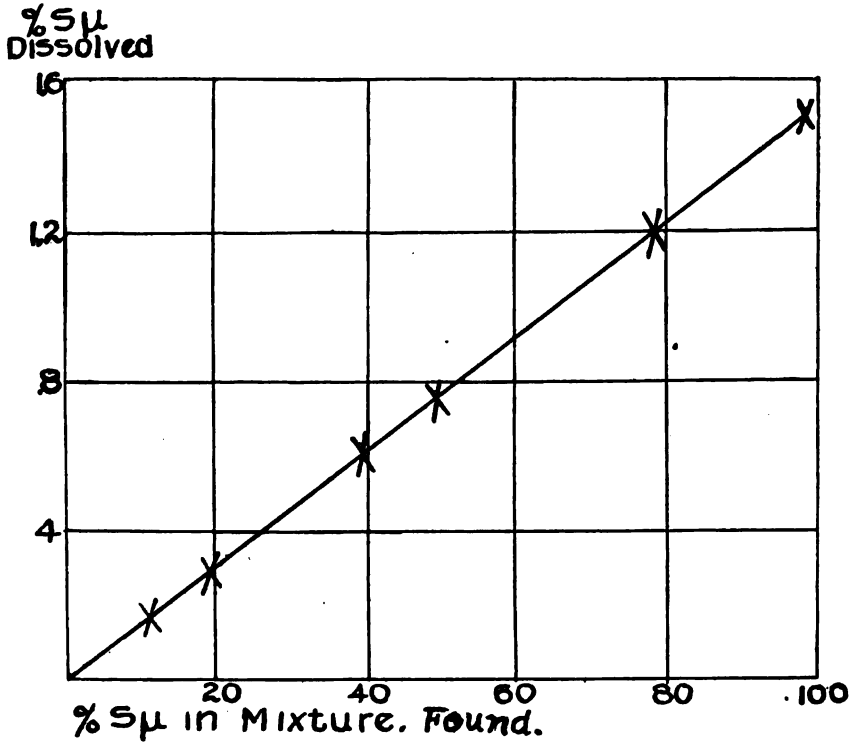


FIG. I.

makes little progress during even months of waiting has been shown by Berthelot[1], Deville[2], Smith and Holmes[3], and by the results of our own experiments.

I. Preliminary Experiments

Sulphur is precipitated in a number of reactions, but some of these, such as the interaction of sulphur monochloride with water, in consequence of the immiscibility of the materials, do not lend themselves to the maintainance of definite concentrations or fixed temperatures during the action. In other cases, such as the decomposition of polythionates, the yields of sulphur are too small. Most of these preliminary experiments, therefore, were made with four actions: *viz.*, that of sulphurous acid and hydrogen sulphide (par. I below) that of polysulphides with acids (par. 2 below), that of sulphides with bromine and iodine (par. 4 below), and that of

[1] Compt. rend., 4, 313, 378.
[2] Ann. chim. phys., (3) 47, 94.
[3] Z. physik. Chem., 42, 469.

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sodium thiosulphate with acids (par. 5 below). It will be seen later that even of these four, only the last two were subjected to the most complete quantitative investigation.

1 Sulphur from Interaction of Sulphurous Acid with Hydrogen Sulphide.—The sulphur obtained by saturating water successively with sulphur dioxide and hydrogen sulphide, did not quickly become pulverulent. On the contrary, it was very viscous and was also rapidly oxidized by the air. When this sulphur was allowed to stand for eight days, or until thoroughly hardened, the average composition was 79 per cent. S_μ and 21 per cent. S_λ. After the more rapid hardening process, by grinding with carbon disulphide and acetone, and drying in absence of air, the average proportion of S_μ was 82.6 per cent.

In these experiments the concentration of the interacting substances varied extensively during each experiment, and differed greatly in different experiments. The experiments are mentioned, therefore, simply because the result is interesting in view of the familiar nature of the action. The maintenance of constant concentrations during the interaction for example, by mixing solutions of the gases, involved the use of such enormous volumes of liquid, in order that sufficient amounts of the product might be secured, that further study of this action was not undertaken.

2. Sulphur from Interaction of Polysulphides With Acids.—Calcium polysulphide was prepared according to the method described in Graham Otto's "Anorganische Chemie." Freshly slaked lime was boiled for several hours with flowers of sulphur and after cooling, the solution was filtered. By this means, a 2.5 normal solution of calcium polysulphide was prepared. A solution of sodium polysulphide of approximately equivalent concentration was prepared by boiling the pure commercial sodium sulphide with flowers of sulphur. In these experiments, the acids were added to separate portions of the polysulphide solutions. The following table shows the concentration (2.5 normal) and composition of the polysulphide, the nature of the acid, and the proportion (corrected) of insoluble sulphur found:—

Polysulphide	Acid used and its quantity	% S_μ
2.5 N Ca S_x	Acetic, 33 percent., in excess.....	0.0
" "	" glacial, in excess	0.0
" "	Hydrochloric, 6 N, solution still alkaline.	0.0
" "	" 6 N, in excess	0.8
" "	" 12 N, " "	2.4
2.5 N Na_2S^x	" 6 N, " "	0.5

In each of the above cases an almost pure white powder was precipitated. When the order of mixing was reversed and the polysulphide was added to the acid, hydrogen polysulphide was formed. It is seen from the above results that sulphur containing a measurable, though quite small, content of the insoluble variety may be precipitated from a polysulphide by using an excess of acid.

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3. So-called "Soluble" or "Soft" "Amorphous Sulphur" and Its Properties.—The sulphur formed from polysulphides is often described as "soluble amphorous sulphur[1]," and is thereby distinguished from soluble rhombic or monoclinic sulphur, on the one hand, and from insoluble amorphous sulphur on the other[2]. This sulphur is indeed almost white, instead of yellow but that is evidently a result of fine subdivision. Professor J. P. Iddings, whom we desire here to thank for the interest he shows in the problem, was kind enough to examine this sulphur with the polarizing microscope. When first precipitated, this sulphur consists of minute fluid globules[3] which are wholly isotropic. While they are being watched they become crystalline without altering noticeably their spherical form. At this stage each globule is composed of a mass of elongated crystals radiating from the center of the sphere, each part of the mass showing extinction and illumination independently of the other parts, as the sphere is rotated by turning the stage. While these phenomena are being observed, the whole globule, still without altering its spheroidal form, suddenly turns into a single, transparent, homogeneous crystal with four positions where extinction takes place throughout the whole sphere simultaneously.

The substance after hardening is therefore not optically amorphous at all, although, so far as could be seen with a magnifying power sufficient to show the other phenomena with perfect distinctness, the form is perfectly spherical. This so-called soluble amorphous sulphur (from polysulphides) is consequently nothing but rhomboid sulphur[4]. If, as seems probable, the substance thus passes through the fluid and the monoclinic crystalline stages, both at the temperature of the room, before reaching that form in which it is alone stable at such a temperature, it affords a striking illustration of Ostwald's "Gesetz der Umwaldlungstufen[5]."

4. Sulphur From the Interaction of Normal and Polysulphides With Bromine and Iodine. (Preliminary Experiments.)—The results obtained in paragraph 2. of this section showed that it would be impossible to obtain more than a few percent. of insoluble sulphur by treating polysulphides with acids, owing to the fact that if very concentrated acid was used, one obtained hydrogen polysulphides.

Since traces of iodine[6] in heated sulphur increased the percentages of amorphous sulphur obtained, and it was known that in the preparation of hydriodic acid, by the reaction of iodine and hydrogen sulphide, sulphur

[1] Berthelot, Ann. chim. phys., (3), 49, 430; Dammer "Handbuch," 4, 207.

[2] Tittinger, Pharm. Post, 27, 297.

[3] Fritzsche, Pogg. Ann., 42, 453.

[4] This conclusion has already been stated by Peterson (Z. physik. Chem., 8, 608) and by Muthmann. (Z. Krystallographie, 17, 342).

[5] Handbuch, 2,2, 444, 458.

[6] Berthelot, Compt. rend., 56, 39; Smith and Holmes, This Journal, 27, 999.

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containing considerable proportions of the amorphous variety was formed, it was decided to try the actions of bromine and iodine, dissolved respectively in potassium bromide and potassium iodide, upon the normal and polysulphides of sodium.

The precipitated sulphur was filtered off and dried and extracted as described above. Some of the results of these preliminary investigations are given in the following table.

Source of sulphur	Precipitant	Percent. Sμ obtained
2.5 N Na_2S	2.5 N I	8.0
" "	2.5 N Br	24.0
2.5 N Na_2S_x	2.5 N I	7.5
" "	2.5 N Br	20.0

The sulphur precipitated by iodine came down quite soft, but not oily, and hardened much more quickly than the sulphur precipitated by bromine.

The reaction of bromine caused a considerable evolution of heat, so these results cannot be considered quantitative. It was decided to reserve this field for further investigations. (Section III of this paper.)

5. Sulphur From the Interaction of Sodium Thiosulphate With Acids. (Preliminary Experiments.)—In the following table are given the results of twelve experiments with different acids, and with different concentrations of the same acid. In all these preliminary experiments, save where the contrary is stated, the acid was simply poured into 100 cc. of the sodium thiosulphate solution.

	Conc. of $Na_2S_2O_3$ (100 cc.)	Precipitant	Sμ
1	4N	50 cc. HCl, conc. (12N)	34.0
2	4N	100 cc. HCl, conc. (12N)	39.2
3	4N (saturated with KCl)	50 cc. HCl, conc. (12N)	19.5
4	4N	50 cc. HCl, 6N	6.5
5	8N	500 cc. HCl, conc. (12N)	96.0[1]
6	(50 g. solid $Na_2S_2O_3$, $5H_2O$)	100 cc. HCl, conc. (12N)	94.6[2]
7	4N	25 cc. HNO_3, conc. (16N)	56.5
8	4N	100 cc. HNO_3, 8N	15.7
9	4N	100 cc. H_2SO_4, conc.	20.2
10	4N	100 cc. H_2SO_4, 12N	21.3
11	4N	100 cc. acetic, glacial	0.0
12	4N	300 cc. " "	0.0

The above experiments show that,

(1.) Contrary to Berthelot's belief, the same sulphur compound may give sulphur wholly soluble (Exps. 11 and 12) or almost wholly insoluble (Exp. 5) in carbon disulphide, according to the precipitant used, and that different concentrations of the same precipitant may give different results (Exps. 1 and 4.)

(2) Contrary to Cloez's belief, a solution which is not alkaline (Exps. 11 and 12), but strongly acid, may give wholly soluble sulphur.

[1] The solution of the thiosulphate was slowly added to the vigorously stirred acid.

[2] The finely powdered thiosulphate was slowly added to the vigorously stirred acid.

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(3) An excess of the precipitating acid is not needed in order that appreciable amounts of insoluble sulphur may be found (Exps. 4 and 7.) That in these cases the 6.5 per cent. and the 56.5 per cent. of insoluble sulphur is not due to the free sulphurous acid liberated by the action, is shown by the negative result in Exp. 12, where much sulphur was liberated and therefore much free sulphurous acid was present.

(4) With sufficiently high concentrations of the acid, the thiosulphate being taken 8N to reduce the amount of water which it introduces into the system, and the solution of the salt being poured into the acid in order that there may be present at all stages of the precipitation the greatest possible concentration of the acid, a practically quantitative production of insoluble sulphur may be achieved.

(5) The concentration of the ionic hydrogen is a factor in the result, for, when the thiosulphate solution is saturated in advance with potassium chloride to repress the ionization of the acid, the percentage of S_μ falls from 34 (Exp. 1) to 19.5 (Exp. 3).

(6) It appears probable that the large thermal effect when sulphuric acid was used (Exps. 9 and 10) was responsible for the relatively small yield of S_μ. An amount of hydrochloric acid chemically equivalent to the amount of sulphuric acid gave almost twice as large a proportion of S_μ (Exps. 1 and 2).

6. *Effect of Temperature.*—In the above experiments no attention was given to the temperature which of course varied in consequence of thermal effects during the precipitation. It was self-evident however that temperature would exert considerable influence.

To learn more definitely the effects of temperature upon the result three experiments were made with solutions previously brought to 0°, 25° and 40°, respectively.

To secure known concentrations and otherwise similar conditions, equal volumes of 2N sodium thiosulphate and 10N hydrochloric acid were taken and were poured simultaneously and with equal speed into a third vessel.

Temperature	0°	25°	40° [1]
Per cent. of S_μ	47.1	34.0	30.8

II. Final Method of Precipitation.

Some of the preliminary experiments, particularly those in which the thiosulphate was added to the acid instead of the acid to the thiosulphate, had shown that, to secure easily formulated results, definite concentrations must be maintained throughout the process of mixing. This could be done only by arranging the two materials so that the quantities to be used were contained in equal volumes of liquid and then by running the two liquids at equal speed into a mixing vessel. It also had been shown

[1] Also see Section IV.

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that definite temperatures would have to be chosen and maintained constant, in spite of thermal effects, during the mixing. When low concentrations were used the thermal effects were negligible and it was sufficient to pour the solutions, at the desired temperature, simultaneously into a vessel in which constant agitation was secured by means of a stirring apparatus. When more concentrated solutions were used the rate of flow of the liquids and the temperature were regulated by means of the apparatus shown in Fig. 2. Two accurate burettes of 50 cc. capacity, and having

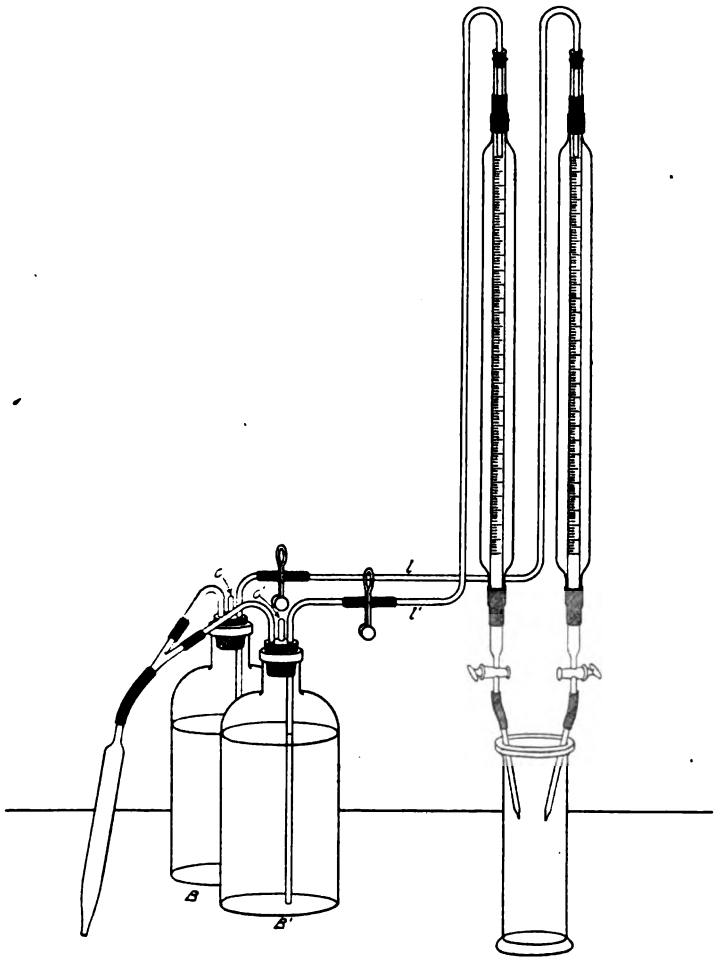


FIG. 2.

scale divisions of almost exactly the same length, were encased in the outer jackets of Liebig's condensers. The solutions contained in B and B' were forced, by means of compressed air, into the burettes through the tubes l and l'. When the pressure was released and C and C' were opened the

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excess of each liquid flowed automatically back into B and B^1 and the burettes were left filled exactly to the zero marks. The liquids in B and B^1 were brought to a temperature close to that desired and water of the proper temperature flowing through the jackets completed the adjustment in this respect. Rapid and complete mixing was secured by the glass stirring apparatus. Complete duplicates were made of almost all the experiments and the data given are means of closely concordant results.

III. Percentages of S_μ in Sulphur Precipitated from Sulphides with Bromine and Iodine.

In these experiments the iodine and bromine were dissolved in aqueous solutions of potassium iodide and potassium bromide, respectively. Two different concentrations of the halogens, and two different concentrations each of sodium sulphide and sodium polysulphide were used. The table shows the concentrations before mixing. The temperature was 0°.

Concentration of Iodine:	Percentage of Amorphous Sulphur				
	2N Na_2S	2.5N Na_2S	5N Na_2S	2.5N Na_4S_7	5N Na_4S_7
2.5 N	.. .	8.4	2.4	7.9	1.5
5.0 N	36.5	43.5	20.3	18.5	15.5
Concentration of Bromine:					
2.5 N	.. .	34.6	30.5	28.7	25.9
5.0 N	.. .	(S_2Br_2)	59.8	(S_2Br_2 + S)	55.9

It will be noted that:

(1) Bromine gives much larger proportions of S_μ than does iodine.

(2) Excess of the halogen, although potent, is not essential to the formation of S_μ.

(3) Equivalent amounts of iodine and the sulphide, both 2.5N, give 8.4 per cent, ; equivalent amounts, both 5N, give 20.3 per cent. ; two equivalents of iodine, *i. e.*, great excess, gives 43.5 per cent. Similar effect of change in concentration is shown by the polysulphide, and when bromine is substituted for iodine.

(4) Excess of bromine gives sulphur bromide.

IV. Percentages of S_μ in Sulphur Precipitated from Thiosulphate with Acids.

Experiments With Hydrochloric Acid.—Many of these experiments were made at 0°, 25°, and at 40°, in order to learn the effect of temperature. In the following tables the first column shows the concentration of hydrochloric acid before mixing; the second and third show the concentration of the acid and of the hydrogen ions (the latter very roughly), at the instant after mixing. The latter figures are calculated on the assumption that the acid is simply diluted with an equal volume of water. The columns following show the percentage of S_μ with various concentrations of sodium thiosulphate. The last column contains remarks on the state of the sulphur when first precipitated.

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At 0°

Conc. of HCl used	Conc. after mixing HCl	Hydrogen Ions	Conc. $Na_2S_2O_3$ and percent. S_μ 2 N	4 N	6 N	State of sulphur from 2N $Na_2S_2O_3$
2N	1N	0.80	6.1	. .	. .	Yellow-brown, viscous, oil
3N	1.5N	1.10	12.4	14.7	8.3	" " " "
4N	2N	1.35	20.4	. . .	. .	More viscous
5N	2.5N	1.55	21.5	18.9	29.6	" "
10N	5N	2.00	47.0	45.9	57.7	Very viscous
12N	6N	2.10	68.8	72.3	75.9	" "

At 25°

Conc. HCl used	Conc. after mixing HCl	Hydrogen ions	Conc. $Na_2S_2O_3$ and per cent. S_μ 2N	4N	6N	8N	State of Sulphur from 2N $Na_2S_2O_3$
2N	1 N	0.80	6.4	. .	3.2	. .	Yellow-brown, viscous, oil
3N	1.5N	1.10	12.9	7.9	7.0	6.6	" " " "
4N	2 N	1.35	13.6	15.9	22.0	25.1	" " " "
5N	2.5N	1.55	22.5	19.1	28.5	39.2	More viscous
10N	5 N	2.00	33.6	52.0	55.9	62.2	Very viscous
12N	6 N	2.10	45.0	67.6	72.4	79.3	" "
*	10 N	1.70	85.6	. . .	. . .	. . .	Non-viscous powder

* This result obtained by mixing 50 cc. of 6N $Na_2S_2O_3$ with 250 cc. of 12N HCl.

At 40°

Conc. HCl used	Conc. after mixing HCl	Hydrogen ions	per cent. S_μ 2N $Na_2S_2O_3$,	State of Sulphur
2N	1 N	0.80	5.5	Yellow-brown, viscous, oil
3N	1.5N	1.10	6.8	" " " "
4N	2 N	1.35	11.9	" " " "
5N	2.5N	1.55	18.5	More viscous
10N	5 N	2.00	30.8	" "
12N	6 N	2.10	34.2	Very viscous

It will be noted that:

(1) The percentages of S_μ is not proportional to the excess of acid, for when there is only an equivalent amount of the latter large quantities of S_μ were obtained, and even when there was excess of the thiosulphate quantities of S_μ up to nearly 40 per cent. were formed. That the S_μ is not due to the sulphurous acid liberated, was shown by the preliminary experiments.

(2) That in a given concentration of the thiosulphate, the percentages of S_μ are directly proportional to the concentrations of the acid after mixing is shown by the straight lines obtained by representing some of the results graphically in Figs. 3 and 5. The abscissae show the percentages of S_μ and the ordinates the concentrations of the acid.

(3) Since the preliminary experiments had indicated a diminution of the S_μ when the ionization of the acid was repressed by means of potassium chloride, the concentration of the hydrogen ion after mixing has also been plotted (Figs. 4 and 6) against the percentages of S_μ[1]. The curves

[1] In view of the work by Oettingen, Z. physik. Chem., 33, 1, upon "The Reaction of Sodium Thiosulphate with Acids," these results seem to show that the percentages of S_μ precipitated from sodium thiosulphate by means of acids may be proportional to the velocity of the precipitation and consequently proportional to the size of the particles precipitated. Consideration of Section V, however, proves any such relationship to be purely incidental.

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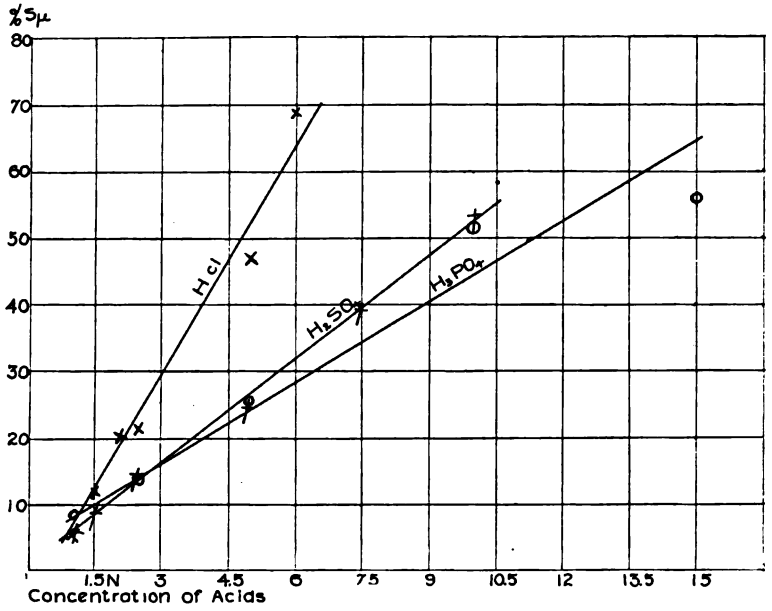


FIG. 3. Twice Normal Sodium Thiosulphate and Acids. 0°

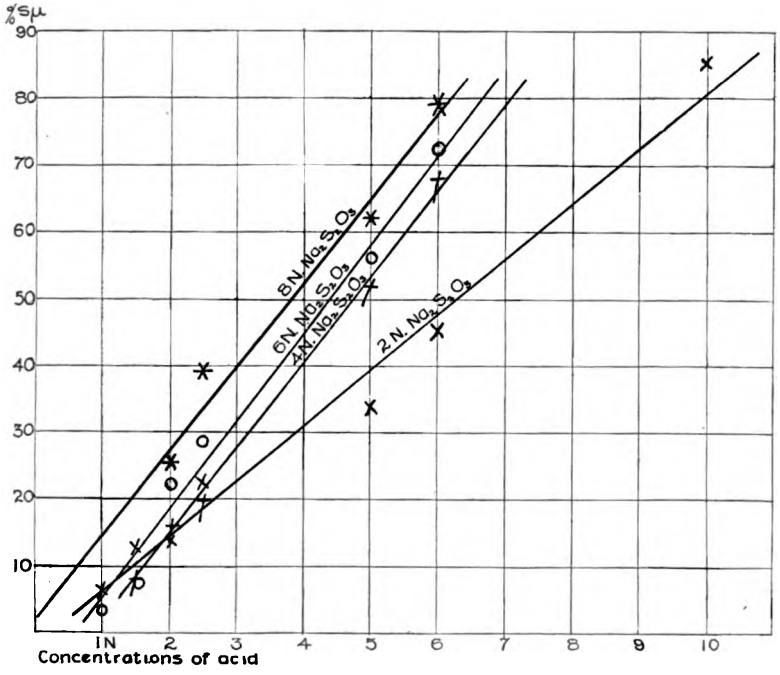


FIG. 5. Sodium Thiosulphate and Hydrochloric Acid. 25°.

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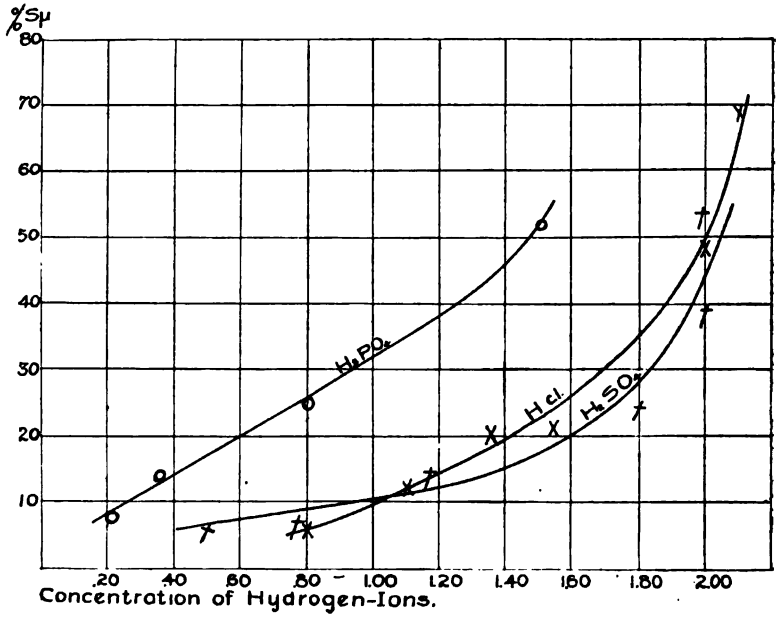


FIG. 4. Twice Normal Sodium Thiosulphate and Acids. 0°.

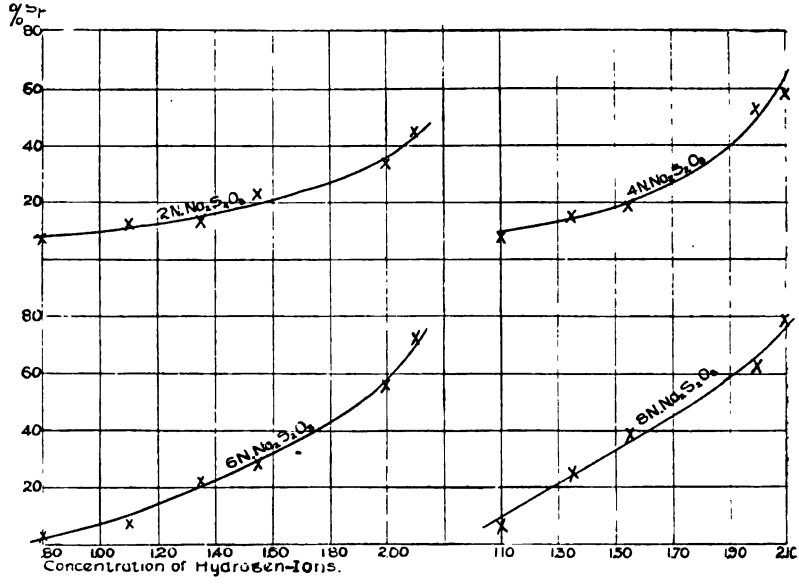


FIG. 6. Sodium Thiosulphate and Hydrochloric Acid. 25°.

indicate that the percentages of S_μ increase more rapidly than the concentrations of the hydrogen ion.

That the concentration of the hydrogen ion is only one factor is shown

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in several ways. For example, at 25°, when the concentration of the acid was very great, and that of the hydrogen ion therefore less than at lower concentrations, the percentage of S_μ was nevertheless the greatest of all (see experiments with phosphoric acid).

(4) When corresponding results at different temperatures are compared, it will be seen that the proportions of S_μ are in general smaller the higher the temperature. This corresponds with the fact that S_μ when once hardened is more permanent at lower temperatures.

Experiments With Sulphuric and Phosphoric Acids.—The data in the following table are stated in the same way as for hydrochloric acid. The temperature was 0°.

At 0°

Conc. of acid used	Sulphuric acid Conc. after mixing H_2SO_4	Hydrogen ions	Percent. S_μ 2N $Na_2S_2O_3$	Phosphoric acid Conc. after mixing H_3PO_4	Hydrogen ions	Percent. S_μ 2N $Na_2S_2O_3$
2N	1 N	0.50	6.5	1 N	0.21	8.1
3N	1.5N	0.76	8.7		. ..	. .
5N	2.5N	1.16	14.4	2.5N	0.36	14.0
10N	5 N	1.80	24.4	5 N	0.80	25.0
15N	7.5N	2.00	38.7		. ..	.. .
20N	10 N	1.99	53.0	10 N	1.46	52.4
30N		. ..	.. .	15 N	. ..	55.9

It will be noted that:

(1) For the observations with sulphuric acid, and for those with phosphoric acid excepting the last of the series, the percentages of S_μ are closely proportional to the concentration of the acid.

(2) Although 2N sulphuric acid gives about the same proportion of S_μ as does 2N hydrochloric acid (6.5 and 6.0 percent. respectively), yet the proportion does not afterwards rise nearly so rapidly with increasing concentrations of the former acid.

(3) Comparing the effects of mixtures isotonic in respect to hydrogen ions we find that the results with sulphuric acid are not very regular. Phosphoric acid gives, however, unexpectedly large proportions of S_μ, approximately twice as great as those given by hydrochloric acid. The highest concentration of sulphuric acid, like the highest hydrochloric acid, although furnishing a relatively small concentration of hydrogen ions, gives by far the greatest percentage of S_μ.

V. By which Conditions and at what Stage is the Percentage of S_μ Determined?

The work in the preceding sections having shown that fairly constant results could be obtained with constant conditions, the next problem was to ascertain which of these conditions determined the proportion of S_μ ultimately found. In particular, is the proportion of S_μ determined by the proportion of the interacting substances and at the

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instant of liberation, or is it determined by a contact action of the resulting liquid mixture upon the sulphur, and during the process of hardening? An answer to these questions was sought by separating the sulphur, within a few moments after the precipitation from the original liquid and substituting for this during the period of hardening, either pure water, more concentrated hydrochloric acid than that used in precipitating, or ammonium hydroxide solution.

Results of Contact Experiments.—Specimens of precipitated sulphur which tended to remain fluid for a considerable length of time were required and the most favorable material for the purpose is that formed by mixing equal volumes of 2N sodium thiosulphate with 2N or 3N hydrochloric acid. The sulphur was precipitated as in Section II, and the liquid was immediately poured off. The acid, water or ammonia was then quickly poured into the sulphur and the materials were violently stirred together. For the purpose of comparison, experiments were made under identical conditions, in which, however, the specimen of sulphur remained in contact with the original liquid.

Conc. HCl with 2 N $Na_2S_2O_3$	Original Liquid		Sulphur in contact with 6N HCl		12N HCl	
	Time	Percent. S	Time	Percent. S	Time	Percent. S_μ
2N	1 day	5.0	1 day	24.1	2.5 hrs.	45.1
	10 days	6.0	1 day	36.2	2.5 hrs.	47.8
					10 days	53.4
					10 days	65.6
3N	10 days	11.8			10 days	51.7
	10 days	12.4				

Sulphur precipitated with 2N HCl and left for 10 days in contact with pure water gave 0.6 per cent. S_μ. The same, left in contact with ammonium hydroxide for 10 minutes or 5 minutes, and then washed, gave 0.2 and 0.3 percent. S , respectively.

It will be observed that where the sulphur remained in contact with the original liquid, the duplicate results are concordant, and agree closely with those obtained at 0° in Section IV. The lack of concordance in the duplicate experiments in which stronger acid was mixed with the sulphur are due to the unavoidable absence of constancy in the process of mixing.

It was observed that in every case where water or an acid was allowed to remain in contact with the liquid sulphur a considerable amount of hydrogen sulphide was formed, a fact which shows the decided chemical activity of this less stable form of sulphur.

The immediate conclusions from these experiments are:

(1) That contact with strong hydrochloric acid increases the yield of S_μ, and that the amounts produced are of the same order as those obtainable when the stronger acid is used for the original precipitation (see Section IV).

(2) That a very brief contact produces almost as great an effect as prolonged contact.

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(3). That when ammonium hydroxide is used, the oily sulphur instantly crystallizes and retains only a trace of S_μ.

(4) Taking into consideration previous experiments we conclude that the percentage of S_μ is jointly determined by the nature and concentration of the precipitants, and by the nature and concentration of the materials remaining in contact with the sulphur.

The Theory of Sulphur Precipitation.—The increase in the yield of S_μ resulting from contact of the oily sulphur with strong hydrochloric acid, during hardening might be explained in two ways.

The oily sulphur may originally contain more S_μ than the largest proportion of amorphous sulphur obtainable from it, and contact with stronger acid must then reduce the speed with which reversion to S_λ takes place and permit the survival of the larger percentage of S_μ. On the other hand, the stronger acid may really increase the yield of amorphous sulphur by converting S_λ into S_μ.

The latter supposition is supported by Berthelot's[1] statement that soluble sulphur becomes in part soluble when allowed to stand in acid liquids. But Smith and Holmes[2] repeated Berthelot's work with an improved method of analysis, and were unable to discover any such effect. It was easily conceivable, however, that while the relatively coarse grained sulphur obtained by pulverization was unaffected, the very finely divided sulphur produced by precipitation might be changed to a marked extent. The soluble sulphur precipitated from sulphides, after solidification, was therefore allowed by us to stand for periods up to thirty days in concentrated (12N) hydrochloric acid and in 6N sulphuric acid. In no case, however, was even a trace of insoluble sulphur produced by this treatment. Nitric acid oxidized this finely divided sulphur so rapidly that it was not used. We believe, therefore, that soluble sulphur, *after it has once solidified*, is not changed into insoluble sulphur to the slightest extent by these substances.

That this solid S_λ, or even the droplets of soluble sulphur before solidification, can be so changed seems theoretically very improbable. In the equilibrium $S_\lambda \rightleftharpoons S_\mu$, the proportion of S_μ at 20° is practically zero. A catalytic agent, (contact agent) would only bring the proportion nearer to that proper to the equilibrium, and would not increase the amount of S_μ. If hydrochloric acid actually operated so as to increase the amount of S_μ it could do so only by playing the rôle of a regular component of the system. That iodine does play such a rôle and does displace this equilibrium in molten sulphur has been shown by Smith and Carson[3], but the displacement is small at the lower temperatures. Here we have

[1] Ann. chim. phys. (3) 498, 442.
[2] This Journal, 27, 1003, or Z. physik. Chem., 54, 282.
[3] Z. physik. Chem., 57, 692.

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to account for an apparent raising of the proportion of S_μ from zero to values often over 50 per cent., and in one case to 96 per cent. The alternative explanation, that much S_μ is contained in the freshly precipitated fluid sulphur and that contact with concentrated hydrochloric acid retards the reversion to S_λ and enables more S_μ to be secured, is theoretically more plausible and can be shown also to accord better with the facts.

The explanation which seems most probable may be stated thus:—In accordance with the principle of "Umwandlungsstufen," the sulphur at the moment of liberation is all in the least stable form, namely that of S_μ. In pure water, or in an alkaline liquid, the droplets, (or the fluid, if the droplets flow together) then pass successively through the stages fluid S_μ, fluid S_λ solid monoclinic sulphur, solid rhombic sulphur:

$$S_\mu \text{ (liq.)} \rightarrowtail S_\lambda \text{ (liq.)} \rightarrowtail S_{\text{monocl.}} \rightarrowtail S_{\text{rh}}$$

When a retarding catalyser such as hydrochloric acid is present in excess, or is quickly mixed with the S_μ, the change to S_λ is retarded and much of the S_μ hardens to amorphous sulphur (super-cooled S_μ). That even with equivalent amounts of sodium thiosulphate and hydrochloric acid about 5 per cent. of S_μ survives, while with sodium polysulphide and the same acid or sodium thiosulphate and acetic acid in equivalent amounts none is obtained, seems to show that the nature of the interaction plays a part, although a subordinate part, in the result.

That in molten sulphur the rate of reversion of S_μ to S_λ may be markedly diminished by hydrogen chloride, phosphoric acid and sulphur dioxide, and the survival of S_μ in the amorphous form made possible was shown by Smith and Holmes[1]. Contrariwise, the accelerating effect of ammonia was noted by the same observers. These effects were studied in greater detail by Smith and Carson[2]. It is justifiable, therefore to attribute the survival of S_μ and the production of amorphous sulphur in precipitation to the same cause as has already been shown to operate in the chilling of strongly heated, molten sulphur. The assumption that the precipitated sulphur is at first wholly S_μ is justified by the theory, and by the fact that in one experiment (Section I, 4) as much as 96 per cent. was actually isolated as amorphous sulphur. The contact actions of differing concentrations of hydrochloric acid (or of iodine in Section III) determine the degree of retardation of the change to S_λ and therefore the proportions in which soluble, rhombic sulphur, and insoluble, hardened S_μ enter into the final product of precipitation. The intermediate formation of monoclinic sulphur (or perhaps one of the other unstable, crystalline forms) suggested in the scheme is supported by the polariscopic observations described in Section I, 3.

Supplementary Experiments.—It was thought that confirmation of the

[1] Ibid., **57**, 688.

[2] Z physik. chem., **57**, 692.

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above view might be obtained by taking the freshly precipitated oily sulphur and chilling it with liquid air. Two specimens were placed in liquid air for 2½ hours. Both became at once perfectly hard. One was ground repeatedly in a mortar under liquid during this time. When allowed to become warm again, however, both specimens returned to the oily condition, and, being now free from acid, eventually gave almost pure soluble sulphur (amorphous sulphur 0.3 and 1.8 per cent, respectively). Apparently, therefore, the hardening which marks the transition from liquid S_μ to amorphous sulphur cannot be hastened by cooling, so that proof that the oil is S_μ was not obtainable in this way.

Another interesting question presented itself. This was whether, in a sample yielding a medium per cent. of amorphous sulphur, during the change of the S_μ to S_λ on the one hand and to hardened, amorphous sulphur on the other. The phenomenon consists in a complete change of certain droplets of S_μ (as wholes) into S_λ and of certain others into amorphous sulphur, or whether each droplet solidifies to a mass made up of a certain percentage of each. We attempted to repeat the polariscope observations described in Section I, *3*, using, however, a suspension of precipitated sulphur, which should have given a considerable proportion of amorphous sulphur, instead of one giving only pure soluble sulphur. We have again to thank Prof. Iddings for cooperating with us in these experiments. The droplets were examined just after precipitation, and again after standing for 10 days, to determine whether each particle contained some amorphous sulphur, or whether some consisted wholly of this form and others contained none. The hardened material was also treated with carbon disulphide under the polariscope, to determine whether some particles were wholly soluble, and others insoluble, or whether parts of every one were attacked. Unfortunately, the droplets obtained under conditions which give amorphous sulphur are so small that no definite conclusion could be reached with instruments which showed the effects already described with perfect clearness.

Summary of Results.

1. Berthelot's and Cloez's rules do not give a correct formulation of the facts, inasmuch as polysulphides do yield S_μ when treated with concentrated active acids, but with dilute acids yield no S_μ.

2. The so-called "soluble" or "soft" "amorphous sulphur" formed by precipitation from polysulphides is not amorphous but is actually crystalline sulphur.

3. There has been devised a method of precipitating sulphur, with concentrations and temperature remaining constant during the precipitation, and this method gives constant results.

4. The proportions of S_μ formed when iodine and bromine interact with sulphides and polysulphides have been studied quantitatively.

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5. The proportions of S_μ when acids, such as acetic, phosphoric, sulphuric and hydrochloric interact with sodium thiosulphate have been studied quantitatively.

6. With acetic acid and the thiosulphate no S_μ is produced, with the other acids the percentages of S_μ is in each case proportional to the concentrations of the total acid in the mixture at the moment of precipitation.

7. The concentration of ionic hydrogen seems to be a factor in determining the proportions of S_μ, but it is evident that they determine it jointly with other factors which have not yet been determined.

8. It has been shown that the proportion of amorphous sulphur produced by precipitation is determined in part by the nature of the interacting materials, but that a contact effect of the whole liquid in which the liberated sulphur is suspended exercises a still greater effect. The conclusion is that the freshly liberated sulphur is initially all S_μ, and that the reversion to S_λ is retarded during the hardening by the contact action of the acid or halogen in the liquid, different concentrations of the contact agent permitting differing proportions of S_μ to overcome the tendency to revert and thus to remain finally as amorphous sulphur. In conclusion, I desire to thank Professor Alexander Smith for all of his kindly assistance during the progress of this investigation.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS].

SOME NEW FORMS OF APPARATUS.

BY WILLIAM M DEHN.

Received April 27, 1907

When a drop of pure mercury is placed in a clean tube whose internal diameter is less than 3 mm. the metal assumes and retains a cylindrical form owing to the tension exerted by the mercury surfaces not in contact with the glass. The cylinder of mercury may then act as an air tight piston, possessing very easy mobility[1]. A difference of gas pressure on the two ends of the cylinder results in a movement of the mercury until equilibrium is established, the slight friction of the mercury on the glass and the inertia of the mercury being readily overcome by gentle tapping at the end of the tube or on the glass above the mercury drop. Some of the following experiments have shown that this drop of mercury is sensitive to a difference of pressure less than 0.1 mm.

Hygrometer.—The apparatus is constructed as follows:—The bulb C made from a small flask (20-50 cc.) is attached first to the stopcock B and then to the side-tube D. This side-tube is made from a 1 cc. pipette graduated to 0.01 cc. and must have an internal diameter less than 3 mm. The apparatus without A attached is weighed empty and is then filled with

[1] Z. physik. Chem. 11, 587.

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water (including the hole of the stopper B) to a readable distance on the graduated scale D. After weighing, the volume of the bulb C to the first mark on the scale of D, plus the volume of the boring of B, may be calculated. After calibrating in this manner, the 2 cc. finely-graduated pipette A and its funnel are attached.

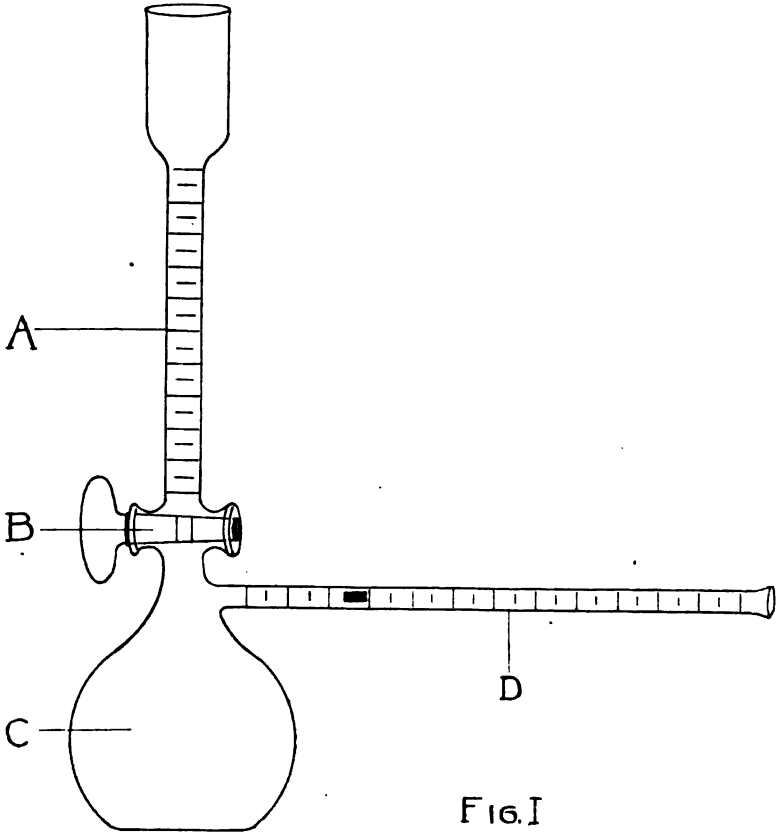


FIG. I

Methods of Using.—Method (a). The apparatus, after being properly cleaned by washing successively with water, alcohol, and ether, is dried by drawing air through the tube A. It is then filled with air to be tested. This is easily done by aspirating at the top of A while repeatedly and successively stopping the end of D, closing the stopcock B, opening the end of D and opening the stopcock B.

The drop of mercury (3 mm. or more in length) is placed in the end of D and is caused to move along the scale toward the zero point near[1] the

[1] Clean, dry mercury should be used. It is conveniently kept in a small flask whose neck is drawn out to a moderately small capillary tube. From this a regulated quantity of mercury can easily be poured out.

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bulb C. The stopcock B is closed and the correct position of the mercury drop is regulated and read. Concentrated sulphuric acid is then placed in the pipette A to a readable height, and, after draining down[1], the position of its meniscus is read. The acid is then carefully admitted so as to cause the mercury to move toward, and lodge near the center of the to cause the mercury to move toward, and lodge near the center of the tube D; the moisture contained in the confined air is quickly absorbed, the air-volume of C being correspondingly decreased. After 1-2 minutes the final positions of the mercury drop and of the meniscus of the acid are read.

Calculation,—Let C equal the volume of the bulb C plus the stopper boring; c the volume of air in D when the mercury does not start at the zero point; and s the volume of sulphuric acid admitted. Now if the air were perfectly dry, the volume occupied by the contained air and sulphuric aid would be C+c+S. But moisture (w) contained in the air is absorbed by the sulphuric acid and decreases the volume to C+c+S—w the quantity w being most easily calculated by subtracting the difference of the mercury readings from the difference of the sulphuric acid readings. Therefore, the per cent. of moisture of the air is 100w/C+c; and the aqueous pressure (a) is

$$a = \frac{wp}{C + c} \qquad (I)$$

wherein p is the corrected atmospheric pressure at the time of the experiment.

Method (b). Here water instead of sulphuric acid is admitted to the bulb C; the vapor of the water quickly saturates the contained air and proportionally increases the volume C+c. This increase in volume (i), calculated by subtracting the difference of the water readings from the mercury readings, and a table of aqueous vapor pressure give the data necessary for calculating the volume of the moisture, or the aqueous vapor pressure of the air tested. Let W equal the known aqueous vapor pressure at the temperature of the experiment, then the *increase* of aqueous vapor pressure when water is admitted is:

$$a' = \frac{ip}{C+c+i}$$

and the *initial* aqueous vapor pressure is:

$$a = W - \frac{ip}{C+c+i} \qquad (II)$$

Now the sum of a determined by the sulphuric acid method and a' de-

[1] Owing to imperfections of construction, air-bubbles may lodge at the bottom or along the sides of the pipette A; they are easily dislodged by a long, closed capillary tube or by a wire of suitable metal.

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termined by the water method must be equal to the known aqueous vapor pressure, W, at the given temperature, else the two methods described are at fault. The following experiments illustrate not only the accuracy of these two methods but also the sensitiveness of the mercury piston:

Temp.	a	a'	$a+a'$	W
17.5	4.61	10.24	14.85	14.91
19.2	4.70	11.95	16.65	16.57
24.6	11.22	11.48	22.75	22.99
28.3	12.25	16.40	28.65	28.60
4.6	4.50	1.75	6.25	6.35

When the *relative humidity h*, of the atmosphere is sought, the formula:

$$h = a/w \qquad \text{(III)}$$

admits of its easy calculation.

During foggy or misty days apparently greater aqueous vapor pressures than the known vapor pressures at the given temperatures were obtained:

Conditions	Temp.	a	W	p
1. Sleet	—1.2°	8.45	4.20	744.7
2. "	—1.0	8.70	4.26	"
3. Mist	—0.2	6.63	4.51	735.3

Evidently these excesses represent either *supersaturation* or the quantity of finely divided water held in *suspension*; if the latter, the weight in grams in a liter of air (m) can be calculated by means of the formula:

$$m = \frac{a - W(1000)}{p}$$

which gives for the above experiments the following:

1. Mist 5.707 g.
2. " 5.962 g.
3. Fog 2.882 g.

quantities which certainly seem excessive, and suggest rather a preponderance of the condition of *supersaturation*.

Tensimeters.—Form (1). The hygrometer used above may conveniently serve the purpose of a *tensimeter;* in fact in the above experiments its use was that of a tensimeter. Accurate determinations of the vapor pressures of liquids at ordinary temperatures are easily made in the manner indicated; when vapor pressures at temperatures higher or lower than room-temperatures are desired, or when accurate hygrometric determinations are to be made, a rubber tube extension on D will permit of the tensimeter being immersed to the necessary depth in a water-bath whose temperature may be controlled by a thermostat and a stirrer. With this *open* tensimeter, the following determinations were made:

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Substance	Temperature	Vapor pressures Found	Known
Benzene	26.4°	99.80	100[1]
Brombenzene	26.3°	3.90	4[1]
Acetic Acid	30.0°	20.20	20.0–20.6[2]
Ethyl Acetate	30.0°	117.80	118.7[3]
Benzyl Chloride	41.1°	1.82	
" "	50.2°	2.66	
" "	60.1°	10.26	
" "	70.0°	16.56	
" "	80.0°	23.76	
Benzal Chloride	60.0°	4.03	
" "	70.0°	6.57	
" "	90.0°	11.00	
Benzotrichloride	60.0°	1.88	
" "	70.0°	9.65	
" "	80.0°	10.90	
" "	90.0°	18.38	

Form (2). When the vapor pressures of solids or small quantities of liquids are to be determined, the following form of apparatus are found to be more convenient. The essential difference is a shortened, funnel-like portion A and a stopcock B possessing a wide boring through the stopper. The substance to be tested is introduced directly or better is weighed in a capillary tube, narrow enough to pass through the boring to the proper depth and long enough to be held from without while the lower portion containing the substances is quickly clipped off by a sharp

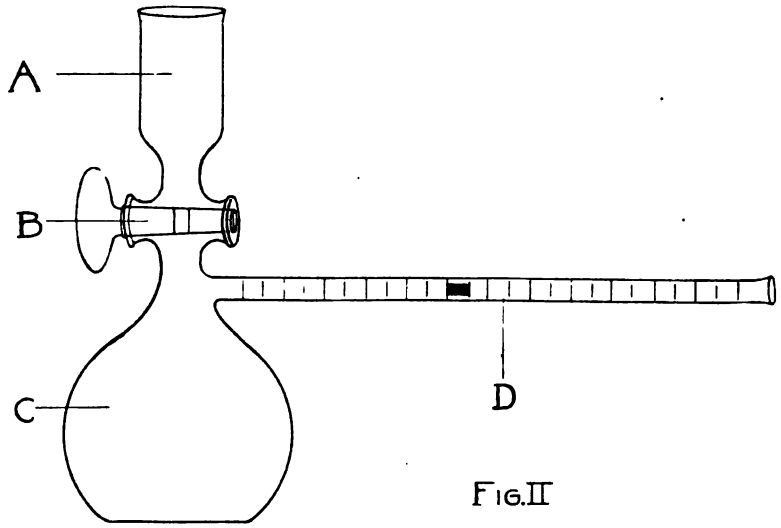


FIG. II

[1] Kahlbaum, Z. physik. Chem., **26**, 603.
[2] Ibid. **7**, 433; **13**, 34; J. Chem. Soc., **49**, 790.
[3] J. Chem. Soc., **63**, 1191

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turn of the stopcock (See Fig. III). The volumes occupied by the glass and by the substance introduced must, of course, be subtracted from C+c, when very accurate results are desired.

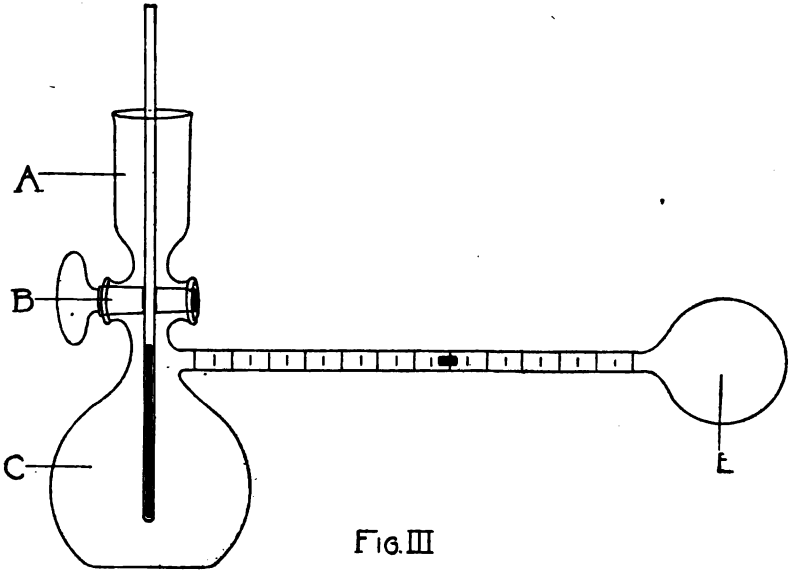


FIG. III

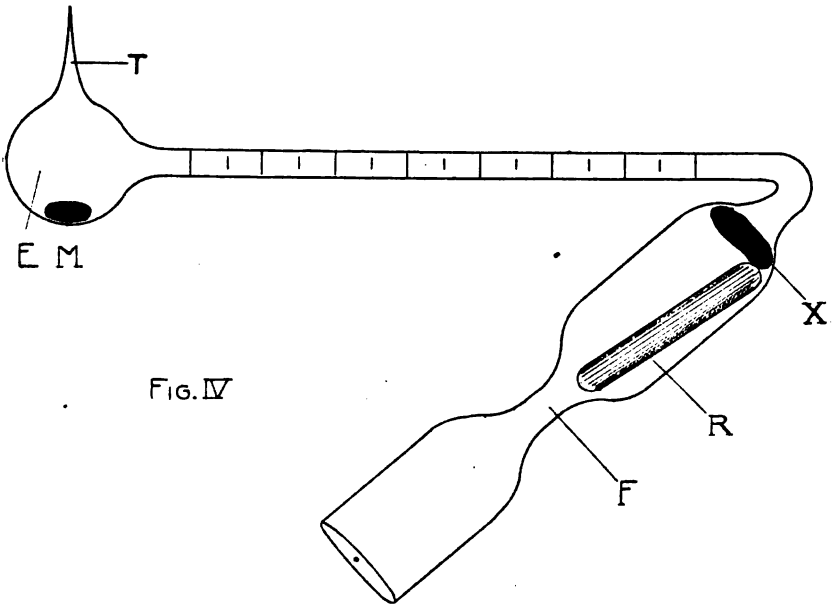


FIG. IV

Since by means of these instruments vapor pressure determinations at ordinary temperatures are easily made, it would seem that these physical constants may often and conveniently serve the purpose of identifying or

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testing the purity of a number of organic compounds. For instance ethyl alcohol and its denaturized product, containing wood alcohol, can now be distinguished more quickly by vapor pressure determinations than by the process of distillation. Of course, convenient tables of vapor pressures at all ordinary tempertures must be prepared; a task which it is intended to undertake in this laboratory.

Forms 3-5. When vapor pressures at high temperatures are desired or when a series of vapor pressures whose determination may extend over periods of time involving changes of atmospheric pressure, are to be made, the following *closed* forms of tensimeter are more convenient; in fact for most purposes the forms depicted in figures IV and V are the most convenient.

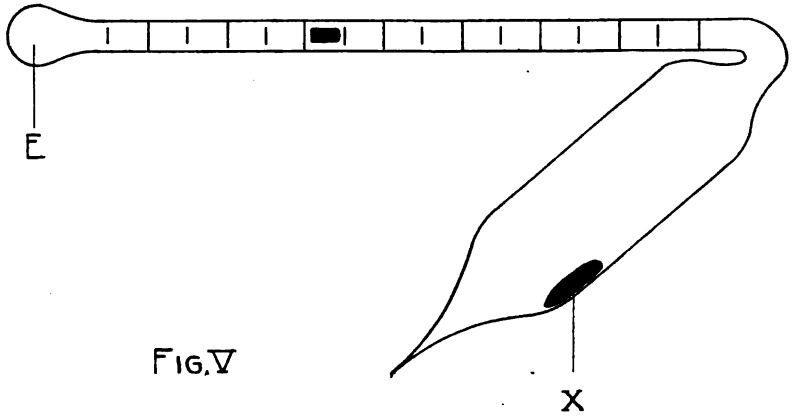


FIG. V

Methods of Using.—After the instruments have been thoroughly dried,[1] the mercury drop is introduced.[2] The substance X, whose specific grav-

[1] The chief difficulty to be guarded against in the use of these closed tensimeters is moisture persistently clinging to the inner surfaces. When the instruments are washed successively with water, alcohol, and ether and are then exhausted by means of the water pump—even while heating in the smoky flame—traces of moisture may remain in the closed end and will exert a most disturbing influence. Backward movement of the mercury when the instrument is first heated indicates the presence of this moisture. Successive washings with water, alcohol, and benzene have given better results than when water, alcohol, and ether have been used. The only safe way, however, is to open the bulb end (E), (See Fig. IV), to heat in the smoky flame and to draw dry air through the apparatus while cooling. The bulb is best opened by heating in one spot, attaching a small hot glass rod and drawing out a capillary tube. This capillary tube, when broken off, will permit of air being drawn through the instrument; and, after drying, can easily be fused off to the rounded surface of the bulb.

[2] When the form shown in Fig. V is employed the end E may be calibrated by first bringing the mercury into this end, and reading the scale; then bringing the mercury into the middle of the scale and reading its volume. When larger bulbs E are used they may be calibrated by filling with mercury to a mark on the scale and then all of the mercury is poured out and weighed. A calibration of the side containing the substance, in figures IV–VI, is easily made after the apparatus has been used. The fused end is cut off sharply and the instrument is emptied and cleaned; then some water from a finely-calibrated burette is first run in and by aspirating gently is caused to rise on the graduated scale to a readable distance. Finally enough water from the burette is dropped in to fill flatly the substance-side and the portion of it cut off.

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ity must be known, is weighed and introduced through the funnel-like portion F shown in Fig. IV. The constriction of this funnel is then carefully narrowed in the flame to a mere capillary tube. While cooling, the atmospheric temperature (t) and the corrected atmospheric pressure (p) are read. The position of the mercury drop is carefully regulated by tapping, and, while holding the instrument so as not to heat it above the room temperature, the capillary tube is quickly sealed off in a narrow flame. The *position* of the mercury drop and its *volume* are read, then the instrument is heated to the successively higher temperatures (t') and the resulting positions of the mercury are read and recorded.

Calculation.—In Fig. VI let a equal the air volume of the air-cushion side, let c equal the air of the side containing the substance X and let b equal the increase of volume of c (and the decrease of volume of a) when the mercury is moved by the additional vapor pressure of X. Now when the tube is heated and X contributes no increase of vapor pressure, the position of the mercury remains unchanged. Though remaining equal the pressure (p') on both sides of the mercury are increased in value as

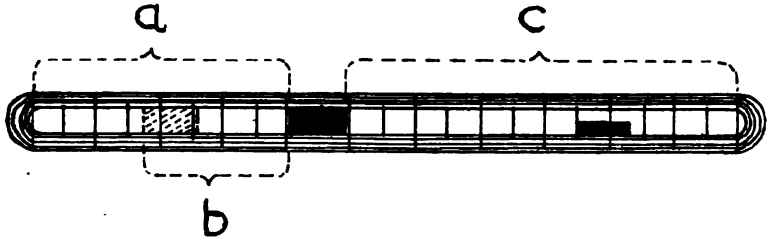


FIG. VI

shown in the equation, $p'=t'p/t$. When X contributes pressure, the mercury moves along to the new position and a decreases in volume to $a-b$; the pressure (p'') now in this side is indicated by the equation:

$$p'' = \frac{a}{a-b} \times \frac{t'p}{t}, \text{ or } \frac{apt'}{(a-b)t} \qquad \text{(IV)}$$

The increase of tension in c, as shown by the movement of the mercury, has resulted from the increase of volume (v) of the vapor in c; the volume occupied by this vapor can be calculated by means of the equation:

$$v = \frac{(a+c)b}{a} \qquad \text{(V)}$$

Now since the volume occupied by this vapor, plus the original air, is equal to $c+b$, the pressure (p''') exerted by the vapor is equal to $\frac{v}{c+b}$ times the pressure (p''), in the other, or the air-cushion side. This is expressed:

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$$p''' = p'' \frac{v}{c+b}$$

By substituting in this equation the values of p'' and v derived from the two preceding equations:

$$p''' = \frac{a}{a-c} \times \frac{t'p}{t} \times \frac{(a+c)b}{a} \times \frac{1}{c+b}$$

or

$$p''' = \frac{(a+c)\,bpt'}{(a-b)(c+b)t} \qquad \text{(VI)}$$

an equation is thus obtained which admits of easy calculation of vapor pressures of liquids and solids, exerted in these closed forms of apparatus.

Since a, c, p, and t are constant in a series of determinations with the same instrument, the factor $\frac{(a+c)p}{t}$ can be calculated and its value k may be substituted in the above equation:

$$p''' = \frac{kbt'}{(a-b)(c+b)} \qquad \text{(VII)}$$

In experiments involving water or substances effected by water, *the aqueous vapor pressure of the air* contained in the substance-side must be taken into consideration, if accurate results are desired. The aqueous vapor in the air-cushion side may be ignored, because, at ascending temperatures, this vapor will behave like air itself. In respect to the aqueous vapor pressure on the substance-side, four possible cases arise; the substance may (1) absorb water; (2) evolve water at room temperature; (3) evolve water only at elevated temperatures; or (4) remain unaffected by water. In the last case, for instance with benzene, chloroform, etc., the aqueous vapor pressure on the substance-side may be ignored because here as on the air-cushion side the water vapor will behave like an equivalent volume of air.

When the substance absorbs or evolves water, a number of methods of manipulation may be employed.

Method (a). The tensimeter may be filled with dry air. This is the absolute method and is conveniently employed as follows: A capillary tube is drawn out from the bulb E (See Fig. IV); the mercury drop M is first introduced, then the glass rod R and finally the substance X. The substance should fill, as completely as possible, a small, *thin-walled,* capillary tube which is to be sealed before being introduced. The two ends of the tensimeter are attached to sulphuric acid wash bottles and air is drawn through the entire apparatus until the contained air is dry. The capillary T is then fused off and the constriction F is drawn down to a small capillary. After cooling, the capillary is quickly fused off, the mercury drop is adjusted along the scale and its position is read; the tube containing the substance is then carefully broken by means of the enclosed rod without disturbing the position of the mercury. When

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the tube containing the substance is *thin-walled,* no difficulty at any stage is encountered in this method.

Method (b). The tensimeter may be filled with ordinary air and the substance may be introduced as in the preceding method. When the tensimeter is filled at low temperatures (0°-11°), errors of vapor pressures equal to 4-8 mm. may be introduced. In many experiments these errors are negligible; however, if they are to be avoided, a determination of the aqueous vapor pressure (z) of the air must be made, and its value must be interpolated in the calculation. This may be interpolated fairly accurately by adding z to the vapor pressures calculated by means of the formula VI, or with entire accuracy by means of the formula:

$$p''' = \frac{(a'+c')(ap+cp-zc)b't}{(a+c)(a'-b')(c'+b')} \qquad \text{(VIII)}$$

which is derived as follows: When z in the substance-side is eliminated by absorption, the volume of air in the entire apparatus is reduced by the factor $\frac{zc}{p}$ and becomes equal to $a+c-\frac{zc}{p}$. The pressure (p^z) then becomes:

$$p^z = \frac{a+c-\frac{zc}{p}}{a+c}\,p \text{ or } \frac{ap+cp-zc}{a+c} \qquad \text{(IX)}$$

which being substituted for p in formula III, now involving a', b', and c', the new readings of the position of the mercury drop, yields equation VIII.

Method (c). The tensimeter may be filled with ordinary air and the substance may be introduced in the exposed condition. Here the substance is introduced directly into the apparatus (See Fig. V.) and the stopcock or the capillary is closed. After standing for some time the tube is quickly opened and closed; this process is repeated until equilibrium is established between the contained air and the substance. Before the final closing, the mercury drop is regulated and its position is read; of course, p and t are determined at this time.

This is a very convenient method of procedure and gives accurate vapor pressures for all substances that evolve water or absorb water (*e. g.,* partially dehydrated salts). It must be remembered, however, that the vapor pressures of substances at the temperatures of sealing are not indicated by this method; only the *relative* vapor pressures above the initial temperature. But as relative pressures are usually desired, and since the pressures at the temperatures of sealing are usually so small that they are negligible, this method is found to be very practicable.

By the use of these closed forms of apparatus, the vapor pressures of a number of hydrated salts have been determined; the data will be given in a future contribution in connection with another subject. The

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experience of a large number of determinations has shown that these instruments possess advantages not completely shared by the Bremer-Frowein[1] and other forms.

(1). They are easily prepared, (2). They are compact, (3). They measure a large range of pressures, (4). They are easily heated, (5). They establish equilibrium rapidly, (6). They are rapid and accurate.

That the instruments are cheaply and easily constructed is sufficiently indicated in the descriptions given above.

In respect to *compactness* and *range* it is easily seen that with instruments only 10-15 cm. in length, pressures exceeding 15 atmospheres may be measured; in fact, the pressure that can be measured is limited only by the tensile strength of the glass used.[2] On the other hand, by making bulb E large in proportion to the volume of D, one can secure any desired degree of fineness of reading; for instance if D is readable to 0.001 cc., the fineness of reading (f) can be calculated by means of the equation:

$$f = \frac{p\mathrm{D}}{1000\ \mathrm{E}} \qquad (\mathrm{X})$$

It is readily seen that the bulb E must be made small (Fig. V) when high pressures are measured; and large, when finely-read, small pressures are measured.

The compactness of these instruments admits of their being heated easily; and quickly brings about a condition of equilibrium between the substance and its vapor. For many purposes the instruments may be heated (slowly of course) in porcelain dishes containing water; for more accurate results, they are placed on the horizontal shelves of water-baths controlled by thermostats and stirrers. For the determination of vapor pressures at higher temperatures, the instruments may be placed on bricks or iron blocks in air baths supplied with mica-plate windows. For accurate determinations at high temperatures, oil-baths, etc., may be employed.

The chief objection to long tensimeters of the Bremer-Frowein type is the sluggishness of establishment of equilibrium. This is owing (1) to the large internal volume, and (2) a tendency to condense water on the mercury—the substance being heated up more rapidly than the mercury. The strong surface-tension of the water condensed on the mercury then retards the establishment of equilibrium, even after a uniformity of temperature has been established in the system. While long heating will, of course, bring about a condition of true equilibrium, short tensi-

[1] Z. physik. Chem., 1, 5; 17, 52.

[2] With the Bremer-Frowein form the height of the instrument must, of course, be greater than the column of mercury sustained by the pressure.

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meters of the mercury-piston type avoid these difficulties and admit of almost immediate establishment of equilibria.

Factors of Error. In the mercury-piston type of tensimeter no corrections for the expansion of mercury need be made; the small expansion incurred is practicably compensated (1) by the *compression* of the mercury at the increased pressure and (2) by the *loss* of mercury incurred by the vapor pressure of mercury. However, if these factors of error are to be taken into consideration, a reading of the volume of the mercury-piston may be made at any stage of the experiment.

At high temperatures it might be supposed that the vapor pressure of the mercury itself will exert an appreciable effect; however, as the vapor pressure of mercury on both sides of the mercury-piston is equal in quantity, it can be shown, both theoretically and practically, that it does not enter as a factor of error.

Air enclosed in salt crystals exerts practically no effect, the instrument itself being filled with air; in instruments exhausted to absolute *vacua,* the air expelled from the lamina of crystals exerts a most disconcerting effect.

Since a loss in volume of the solid or liquid is incurred by its partial or complete vaporization, a factor of correction must be introduced, if absolute precison is desired. The volume of the vapor may be reduced by calculation to an equivalent volume of the solid or liquid and this, really an insignificant factor, may be added to the volume of the vapor. (See equation V).

Molecular Weight Determination. When small quantities of liquids and easily volatilized solids, weighed in capillary tubes, are enclosed in the apparatus depicted in figures IV and V, and the heating is increased and continued until all of the substance is vaporized, the mercury-piston will finally come to a state of rest. When the volume b is read at this point, a calculation of the molecular weight of the substance is possible and may thus practically be determined. The *volume* of the vapor at this (t') and higher temperatures is given in equation V:

$$v = \frac{(a+c)b}{a}$$

the *pressure* under which this vapor is held is given in equation IV:

$$p'' = \frac{apt'}{(a-b)t}$$

therefore, its volume under standard conditions is:

$$V = \frac{b(a+c)}{a} \times \frac{apt'}{(a-b)t} \times \frac{273}{760t'} \text{ or } \frac{bp(a+c)273}{t(a-b)760} \qquad (X)$$

and the molecular weight is:

$$\text{Mol. wt.} = 22.393\ W \times \frac{bp(a+c)\ 273}{t(a-b)\ 760}, \text{ or } \frac{t(a-b)\ W\ 62.37}{bp(a+c)} \qquad (XI)$$

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in which W is the weight of the substance used. It will be observed that this equation is *independent of the final temperature,* consequently the apparatus only needs to be placed in an ordinary air-bath and to be heated above the temperature of complete vaporization. Since upon discontinuing the heating and opening the air-bath, considerable time usually elapses and a marked fall of temperature is incurred, before the mercury-piston begins to move back toward its original position, no difficulty in reading the volume b is met with.

By the use of these instruments the following molecular weight determinations were made:

Substance	B P.	t' (Heated)	Mol. wt. Found	Mol. wt. Theory
Carbon Tetrachloride	76.7	110	152.8	153.6
Ethyl Acetate	77.1	92	86.6	88.0
Ethyl Bromide	131.6	190	191.0	188.0
n-Propyl Iodide	101.7	145	161.6	160.0
Xylene	137.5–142.6	173	108.1	106.0

The above experiments show not only the accuracy of the equation but also the accuracy of the method. When it is remembered that the instrument may not only be constructed (starting with a 1 cc. finely-graduated pipette) but the entire determination may be made within an hour, it may be anticipated that this method will take precedence over some of the more laborious methods. Furthermore, for reasons of (1) compactness of apparatus, (2) ease of construction, preparation and heating, (3) use of small quantities of substance, and (4) the possible simultaneous determination of vapor pressure, of dissociation and of boiling points (see below) this method promises to vie with Victor Meyer's method in practical application.

Dissociation of Vapors. Since some vapors dissociate at temperatures above their boiling points, a *secondary* movement of the mercury-piston is a manifestation of this dissociation and may be made a measure of the same. Calculations of the molecular weights at each of the higher positions of the mercury indicate, of course, the degrees of dissociation. When, on cooling, the mercury fails to return to its original position, a *non-reversible dissociation* is revealed. It must be remembered, however, that if special precautions are not observed on cooling, vapors will condense on the walls of tube D; these may then be passed by the mercury and will partially vitiate the reading of non-reversible dissociation.

Resume.

Instruments involving the moving mercury-drop may, therefore, be used to determine:

(1). Humidity. (2). Vapor pressure. (3). Molecular Weight. (4). Dissociation. (5). Boiling point.

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When the pressure is equal to 760 mm. the boiling point is indicated. Other applications of the moving drop of mercury are being planned.

I am greatly indebted to Mr. Edward O. Heuse for assistance rendered in connection with this investigation.

URBANA, ILLINOIS
April 25, 1907.

THE USE OF TIN AS A CATHODE FOR THE RAPID QUANTITATIVE ELECTROLYTIC DEPOSITION OF ZINC, COPPER, SILVER, CADMIUM AND NICKEL.

BY LAURENCE T. SHERWOOD AND GELLERT ALLEMAN.
Received May 21, 1907.

The high price of platinum, together with other minor considerations, led to an investigation in this laboratory in order to determine if metallic cathodes, other than platinum, could be used for the quantitative electrolytic deposition of carious metals, and, if so, to determine the exact conditions productive of the best results. While it is intended to continue this investigation using other metallic cathodes, especially tungsten, this article has to deal entirely with the tin cathode, and the deposition on it of the five elements named in the title.

Attention is directed to the fact that all the results obtained are published in the tables—none having been rejected.

While not so generally applicable as platinum, it was found that for the estimation of the metals enumerated, tin could be substituted for the more expensive material. The attempt has not yet been made to use this cathode in determining any other of the metals but judging from the work thus far it seems quite possible that it may be used for all of those which are deposited in the metallic state.

Platinum has been regarded as about the only suitable cathode material because of its insolubility and immunity from corrosion, and, of course, these were anticipated as the chief defects of tin. The solvent action of electrolytes was especially feared, but with certain precautions which will be mentioned under the special considerations there was no loss of tin during the determination even with such powerful solvents as sulphuric acid and potassium cyanide. Corrosion of other natures gave no trouble whatever.

The following general facts regarding the care of the dishes may be worth mentioning:

Solutions which have not a solvent action may during the progress of an analysis be heated in them upon a sheet of asbestos (thickness exceeding a quarter inch) or upon an electric stove without fear of oxidizing the tin.

On account of the low melting point of tin the dish cannot, of course,

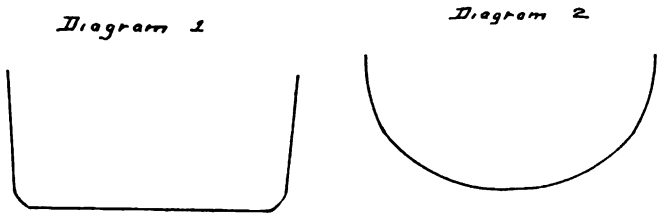
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be held in the free flame nor set upon hot asbestos or an electric stove, if empty.

The surface should be kept bright by an occasional scouring with fairly coarse sea sand.

For reasons which will appear later it is preferable, but not necessary, to keep separate dishes for depositions of each particular metal.

The first dishes were made of Kahlbaum's tin, cast in an iron mold of the shape represented by cross-section diagram No. 1, and cut down on a lathe to a suitable weight, (70-80 grams). The dimensions were: diameter of top, 8 cm.; diameter of bottom, 7 cm.; height, about 3.3 cm. The total inside surface was approximately 115 sq. cm. which was equivalent to about 100 sq. cm. when 100 cc. of liquid was rotating inside. Most of the work on zinc was done with these dishes, but they were unsatisfactory both in their form and on account of pores in their surfaces due to imperfections in the castings. The dish which has thus far given the best results has a form indicated by cross-section diagram No. 2.



These were spun by J. Bishop and Son, from sheet block tin (No. 18 B. & S. gauge) bought of Messrs. Eimer & Amend. The diameter of the top was 9 cm.; the total surface, about 125 sq. cm. which was equivalent to about 100 sq. cm. when 100 cc. of liquid was rotating within. They weighed about 65 grams. Owing to the softness of tin, the edge of the dish where it is grasped by the forceps in weighing should be as thick as consistency will permit.

To economize time the rotating anode was used in practically all the investigations. The forms used consisted of platinum wire respectively 1.4 mm. and 1.1 mm. in diameter, (numbers 17 and 19, B. & S. gauge), bent into spirals. The former size was slightly preferable. The spirals were depressed in the center, conforming somewhat to the shape of the dish. Their diameter was 3.5 cm. The anodes were inserted in the motor shaft. The motors supplied by the Electro-Dental Manufacturing Co., of Philadelphia, were wound to run on a 110 volt lighting circuit and had a speed of 500-700 revolutions per minute. While they answered practically all purposes it is recommended if this form of rotator is used that the maximum speed be at least 1000 revolutions per minute. A lamp resistance could be put in the circuit to diminish this speed to

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any desired. Within the range of speeds used there was hardly a perceptible difference in the character of the metallic deposits.

Zinc. Methods outlined by Exner [1] were adapted for this metal, first using a platinum dish and later tin. With a few exceptions, probably due to some slightly different conditions, his methods served very well. A few experiments showed also that Classen's method, using ammonium oxalate and tartaric acid as electrolytes[2], could probably be used with the tin cathode. However, not enough tests were made to decide conclusively.

Table I records a series of determinations with a platinum dish. The results in Table II were obtained by almost the same method on the tin cathodes described in diagram No. 1. Sodium hydroxide dissolves tin slowly when no current is passing through it and the following procedure is therefore recommended. Prepare the sodium zincate by adding the specified amount of sodium hydroxide (in solid form) to the zinc sulphate solution in a beaker. (It is perhaps worth mentioning that Jena glass should be used in preparing the zincate solution since the strong alkali is apt to dissolve material from the ordinary glass beaker[3]). Place the dish on its support and add thirty or forty cc. of hot water; *close the circuit,* having the rheostat adjusted so that about one ampere will flow as soon as the electrolytes are added; introduce the hot zincate solution; dilute to a suitable volume; adjust the electrodes; start the rotator, and allow the full current to pass in. If this procedure is followed, tin will not be dissolved. With the sodium acetate method it is unnecessary to observe the precaution of having the circuit closed before the electrolyte is added.

The deposits on tin exactly resembled those on platinum. They were crystalline but could easily be washed in the usual manner and weighed. After weighing, the loose material was wiped and brushed out and another determination made by depositing on the remaining coating. Moreover, when once coated with zinc, no precautions were necessary to protect the tin from the solvent action of the sodium hydroxide. The adherent coating was very thin and several depositions could be made before cleaning all the zinc off. To remove the adherent zinc, use dilute hydrochloric or sulphuric acid, or nitric acid with a specific gravity, 1.52. Nitric acid more dilute than this attacked the tin rapidly. After cleaning, the tin surface usually had to be scoured bright with sea sand. Of course the dishes lost a little weight in cleaning but with reasonable care they last indefinitely. Dishes in constant use for a year lost less than two grams.

[1] This Journal, 25, 900.

[2] Ber., 12, 1622.

[3] It must be remembered that Jena glass contains zinc, however, and is somewhat attacked by alkaline solutions. Porcelain would probably be safer.—Editor.

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TABLE I.

$ZnSO_4.7H_2O$ =Zn in gms.	NaOH in gms.	Volume in cc. when diluted	Approximate temp. at start	Current $N.D_{100}$ =A	Volts	Time in minutes	Zn deposited in gms.	Error in pct. of Zn in $ZnSO_4.7H_2O$
0.2496	8	100	65°	5	5	30	0.2490	0.05
"	"	"	"	"	"	"	0.2495	0.01
"	"	"	"	"	"	"	0.2501	0.05
"	"	"	"	"	"	25	0.2502	0.06

TABLE II.

0.2496	8	100	65°	3	7	30	0.2494	0.02
"	"	"	"	"	"	"	0.2501	0.05
"	"	"	"	"	"	"	0.2492	0.03
"	"	"	"	"	"	"	0.2494	0.02
"	"	"	"	"	"	"	0.2494	0.02
"	"	"	"	"	"	25	0.2582	0.13
"	"	"	"	"	"	"	0.2536	0.37
"	"	"	"	"	"	"	0.2515	0.18
"	"	"	"	"	"	"	0.2507	0.10
"	"	"	"	"	"	"	0.2505	0.08
0.2500	"	"	"	"	"	"	0.2508	0.07
"	"	"	"	"	"	"	0.2498	0.02
"	"	"	"	"	"	"	0.2517	0.16
"	"	"	"	"	"	"	0.2495	0.04
"	"	"	"	"	"	"	0.2502	0.02
"	"	"	"	"	"	"	0.2417	0.75
"	"	"	"	"	"	"	0.2448	0.47
"	"	"	"	"	"	"	0.2476	0.22
"	"	"	"	"	"	"	0.2486	0.13

Note: Speed of rotator was 700 R. P. M.

In all the determinations of Table II only two dishes were used and neither of them was cleaned of the adherent zinc after the series was begun. It is quite possible that by depositing upon the porous zinc surface which was formed after the first few determinations a source of error was introduced which may account for the inconsistent results in the latter part of the series and throughout Table IV. This point was not thoroughly investigated but the better results in the first determinations seemed to indicate that that was the case. The irregular results in both Tables II and IV are also probably due to the pores and imperfections in the dishes used. Series V was run on the better form of dish described by diagram No. 2 and the results are consistent. Four or five determinations were made without cleaning off the adherent zinc. It is not advisable to run more than this number in succession.

The time set down by Exner for these depositions was ten to fifteen minutes.[1] Failure to comply with some conditions made it necessary to take a longer time with the sodium hydroxide electrolyte. The bulk of the metal came down in the first few minutes, but traces remained uutil the time stated

[1] See also paper by Ingham, This Journal, **26**, 1272.

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had expired. The time required on tin was the same as that on platinum. As rapidity was not a special object in this investigation no great effort was made to reduce the time although it should not be difficult to do so. Five amperes, the current used on platinum, gave too loose a deposit on the tin, but no longer time was required with three amperes.

Tables III and IV record series on platinum and tin respectively with the sodium acetate electrolyte. This method was adapted with practically no change from Exner's conditions. The deposits in both cases were crystalline and rather loose but there was no difficulty in washing and weighing them.

TABLE III

$ZnSO_4.7H_2O$ =Zn in gms.	$CH_3.COONa$ in gms.	30 per cent. acetic acid in cc.	Volume in cc. when diluted	Approximate temp. at start	Current $N.D_{100}$ =A.	Volts	Time in minutes	Zn deposited in gms.	Error in pct. of Zn in $ZnSO_4.7H_2O$
0.2500	3	0.2	100	20°	3	18.5-11.5	15	0.2509	0.08
"	"	"	"	"	"	"	"	0.2496	0.03
"	"	"	"	"	"	"	"	0.2499	0.01
"	"	"	"	"	"	"	"	0.2489	0.10
"	"	"	"	"	"	"	"	0.2491	0.08

TABLE IV

0.2500	3	0.2	100	20°	2	12.5- 9.5	15	0.2494	0.05
"	"	"	"	"	"	"	"	0.2483	0.15
"	"	"	"	"	"	"	"	0.2505	0.05
"	"	"	"	"	"	"	"	0.2491	0.08
"	"	"	"	"	"	"	"	0.2504	0.04
"	"	"	"	"	"	"	"	0.2474	0.23
"	"	"	"	"	"	"	"	0.2488	0.11
"	"	"	"	"	"	"	"	0.2509	0.08
"	"	"	"	"	"	"	"	0.2484	0.14
"	"	"	"	"	"	"	"	0.2483	0.15
"	"	"	"	"	"	"	"	0.2497	0.03
"	"	"	"	"	"	"	"	0.2513	0.12
"	"	"	"	"	"	"	"	0.2490	0.09
"	"	"	"	"	"	"	"	0.2489	0.10
"	"	"	"	"	"	"	"	0.2517	0.16
"	"	"	"	"	"	"	"	0.2496	0.03
"	"	"	"	"	"	"	"	0.2516	0.15
"	"	"	"	"	"	"	"	0.2480	0.18

Note: Speed of rotator was 700 R. P. M.

The series recorded in Table V was run by Mr. R. L. Hill of this laboratory. He used the tin dishes represented in diagram No. 2 and was careful not to run more than four or five determinations on a particular dish without cleaning off the adherent coating of zinc. He also used a slower rotator (550 R. P. M. instead of 700 R. P. M.) and a slightly smaller anode, which may account for the extra time required.

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TABLE V

$ZnSO_4.7H_2O$= Zn in gms.	$CH_3.COONa$ in gms.	30 per cent. acetic acid in cc	Volume in cc. when diluted	Approximate temp. at start	Current $N.D_{100}$ =A	Volts	Time in min.	Zn deposited in gms.	Error in pct. of Zn in $ZnSO_4.7H_2O$
0.2500	3	0.2	100	20°	2	18-13	17	0.2500	0.00
"	"	"	"	65°	2	14-11	"	0.2493	0.06
"	"	"	"	"	"	"	"	0.2500	0.00
"	"	"	"	"	"	"	"	0.2497	0.02
"	"	"	"	"	"	"	16	0.2496	0.03
"	"	"	"	"	"	"	"	0.2490	0.09
"	"	"	"	"	"	"	18	0.2498	0.02
"	"	"	"	"	"	"	16	0.2496	0.03
"	"	"	"	"	"	"	17	0.2495	0.04

Silver. When silver nitrate solution comes in contact with tin a black deposit forms on the tin. This action is of course objectionable; but if potassium cyanide were first added and the double cyanide formed, it did not take place. However when potassium cyanide was used alone as an electrolyte the silver deposits were dark and loose. The addition of a suitable amount of oxalic acid afforded a reducing action and this difficulty was also overcome, the deposit being the characteristic milk white silver. Unless rather low currents were used the deposits had somewhat more tendency to sponginess than on platinum but if a little clear gelatine solution were added, one and a half amperes could be used.

Potassium cyanide in the dish when no current is passing of course dissolves a small amount of tin, (from one to three milligrams if allowed to stand a minute), but when the tin surface is absolutely clean of oxide or any foreign material the dish does not lose appreciable weight in silver determinations if the circuit is closed before the addition of the cyanide. A number of experiments were made with the potassium cyanide alone in the dish and also with the cyanide and oxalic acid together. Hot water was first put in the dish and the circuit closed, after which the respective amounts of cyanide or mixture of the two reagents that were used for the silver determinations were added. The remaining operations were the same as in the course of a regular analysis.

TABLE VI.

Weight of dish	KCN in grams	Saturated solution of oxalic acid in cc.	Amperes	Time in minutes	Loss of weight
59.8008	2	10	0.6	20	0
65.1525	"	"	"	"	0
63.1403	"	"	"	"	0.0001
64.8920	"	"	"	"	0.0003
63.0190	"	"	1.0	"	0
64.8203	"	"	1.0	"	0

When silver is being deposited it is improbable that tin ever dissolves at all, for the determinations were fully as accurate as any made on the platinum dishes. To prevent possible solution of tin the following pro-

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cedure was observed: the cathode was placed upon its support and hot water added; the circuit was closed, having the rheostat adjusted so that about one ampere would flow when the electrolytes were introduced; oxalic acid, gelatine[1], and the cyanide solution of silver were added in the order named: the volume was diluted to 100 cc.; the electrodes were adjusted, the rotator started and the current regulated. It was not thought that oxalic acid would dissolve tin appreciably when the current is not passing, except on standing. It is certain that it does not when the current is on.

There was no trouble in depositing one layer of silver upon another indefinitely if each time the loose metal were wiped out and the remaining coating well brushed, but it is probably safer not to deposit more than four or five layers without cleaning. When desirable the firm deposit may be cleaned off with potassium cyanide. The action may be hastened by passing a current of about 0.2 amp. through the cyanide, making the dish the anode. The deposit could also be scoured off without the aid of a solvent.

TABLE VII

$AgNO_3$ =Ag in grams	KCN in gms.	Oxalic acid in cc. of saturated solution	Gelatine (1 gm =1000 cc.) in cc.	Volume when diluted	Approximate temp. at start	Current $N.D_{100}$ =A	Volts	Time in minutes	Ag deposited in gms.	Error in pct. of Ag in AgNO
0.2500	2	10	1	100	65°	1.0	6	25	0.2500	0.00
"	"	"	"	"	"	"	"	"	0.2499	0.02
"	"	"	"	"	"	"	"	"	0.2503	0.08
"	"	"	"	"	"	"	"	"	0.2501	0.03
"	"	"	"	"	"	"	"	"	0.2497	0.07
"	"	"	"	"	"	1.5	7	20	0.2502	0.05
"	"	"	"	"	"	"	7	"	0.2504	0.10
"	"	"	"	"	"	"	6.5	"	0.2497	0.07
"	"	"	"	"	"	"	6	"	0.2499	0.02
"	"	"	"	"	"	"	6.5	"	0.2495	0.12
"	"	"	"	"	"	"	6	"	0.2498	0.05

Note: Speed of rotator in first five determinations was R. P. M.; in the last six run by Mr. Hill the speed was 550 R.P.M.

Cadmium. Exner's condition for cadmium[2] applied to the tin cathode with little alteration. Sulphuric acid was the electrolyte and this of course dissolved tin unless the dish was protected by the current. The circuit therefore had to be closed before adding the acid. Experiments showed also that only a small quantity could be used. With more than 1 cc. of acid, specific gravity, 1.115 (conc. acid diluted 1 to 10), the solvent action was more powerful than the tendency of the current to keep the metal at the cathode. But regardless of the solvent action, 1 cc. of the electrolyte gave the best deposits of cadmium. The experi-

[1] The gelatine should be pure and the solution clear. "Isinglass" was the material used.

[2] This Journal, 25, 903.

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ments recorded in Table VIII were made to show the solvent action of different amounts of acid of the specific gravity noted above. The dishes were filled with hot water; the circuit closed; the rotator started, and the acid added from a pipette. The regular procedure of a determination was then followed.

TABLE VIII

Weight of dish	H_2SO_4. Sp. Gr. 1.115 in cc.	Amperes	Time in minutes	Loss of Weight
62.9874	3	5	10	0.0009
64.7832	2	5	10	0.0003
62.9865	1	5	10	0.00

In the experiments of Table IX, made by Mr. Hill, all the reagents were put in the dish before the circuit was closed, except the acid, the addition of which was the final detail of the manipulation. The deposits were crystalline, closely resembling zinc. The adherent coating was cleaned out once in four or five determinations, only the loose material being removed after the other depositions. Sulphuric acid aided by a feeble current dissolved the coatings, or else they were scoured off without using any solvent.

TABLE IX

$3CdSO_4.8H_2O$ =Cd in gms.	H_2SO_4, Sp. Gr. 1.115 in cc.	Volume when diluted in cc.	Approximate temp. at start	Current $N.D_{100}$ =A	Volts	Time in minutes	Cd deposited in grams	Error in per cent Cd in $5CdSO_4.8H_2O$
0.2500	1	100	65°.	5	24-15	10	0.2502	0.04
"	2	"	"	"	"	"	0.2495	0.09
"	1.5	"	"	"	"	"	0.2504	0.07
"	1	"	"	"	"	"	0.2503	0.05
"	"	"	"	"	"	"	0.2499	0.02
"	"	"	"	"	"	"	0.2501	0.02
"	"	"	"	"	"	"	0.2503	0.05
"	"	"	"	"	"	"	0.2500	0.00

Note: Speed of the rotator was 550 R.P.M.

Copper. Copper, although usually most readily determined by electrolytic methods presented considerable difficulty. When a solution of the neutral or slightly acid sulphate was put in a tin dish a black deposit came down. Also, with the common acid electrolytes, loose black deposits resulted in the attempt to separate the metal by a current. Additions of ammonium hydroxide to the sulphate solution prevented the immediate formation of the black coating until the current was introduced but results from this electrolyte were not at all promising, the deposits being dark and loose.

An adaptation of E. Wagner's oxalate method[1] gave fairly good results although considerable manipulation was required. The dish, first of all, should be absolutely free from oxide of any sort, although a deposit may be made upon a surface of bright adherent copper. Then by observance of the following conditions good

[1] Z. Electrochem., 2, 613.

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results may be obtained: Mix in a beaker 55 cc. of saturated ammonium oxalate solution, 5 cc. of saturated oxalic acid solution, and 1 cc. clear solution of pure gelatine (1 gram of gelatine = 1000 cc.). Place the dish on its support, introduce this mixture, start the rotator and add the copper sulphate solution. Without delay close the circuit and dilute to a suitable volume. At the end of ten minutes add from a pipette 10 cc. of oxalic acid solution, at fifteen minutes add 5 cc., and at eighteen minutes, 5 cc. The deposition will then usually be complete after twenty minutes. The solution must be cold at the start, for otherwise the deposit will be black and loose. It is important too that the anode be rotating when the copper solution is added, since occasionally a very adherent blue material formed on it which could not be washed off. If the oxalic acid was not added at the stated times the results were invariably low, slight amounts of copper remaining in solution until the end of about thirty minutes. The deposits were dark red and crystalline but adherent enough to wash and weigh. They were removed by a hot potassium cyanide solution. Series X was run by Mr. Hill.

TABLE X

$CuSO_4.5H_2O$= Cu in grams	Saturated solution $(NH_4)_2C_2O_4$ in cc.	Saturated solution of $H_2C_2O_4$ at start, at 10, 15 & 18 minutes respectively	Volume in cc. when diluted	Approximate temp. at start	Current $N.D_{100}$ =A	Volts	Time in minutes	Cu deposited in grams	Error in pct. Cu in $CuSO_4.5H_2O$
0.2500	55	5+10+5+5	100	20°	5	19-10	24	0.2498	0.02
"	"	"	"	"	"	"	21	0.2495	0.05
"	"	"	"	"	"	"	20	0.2502	0.02
"	"	"	"	"	"	"	20	0.2492	0.08
"	"	"	"	"	"	"	20	0.2502	0.02
"	"	"	"	"	"	"	22	0.2502	0.02
"	"	"	"	"	"	"	21	0.2487	0.14
"	"	"	"	"	"	"	22	0.2498	0.02
"	"	"	"	"	"	"	20	0.2487	0.14
"	"	"	"	"	"	"	21	0.2490	0.11
"	"	"	"	"	"	"	20	0.2492	0.08

Note: Speed of the rotator was 550 R.P.M.

This method while fairly accurate if the conditions are closely observed, requires more manipulation than the methods on platinum. It was observed, too late for an investigation to be undertaken, that from cyanide solutions copper, with a high current density, comes down on tin as a bright and extremely adherent deposit just as it does on platinum. Since the cyanide was a satisfactory electrolyte for the quantitative determination of silver on tin, it is quite probable that it may also be used for copper. A thesis written in 1906 by Miss Anna L. Flanigan at the University of Pennsylvania describes some recent cyanide methods for copper deposition on platinum and it is intended to try and adapt them in this laboratory for use with tin cathodes.

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Nickel. Exner's conditions for nickel [1] served very well for the determination of this metal. There was no decided preference in the use of ammonium sulphate and ammonium hydroxide; or ammonium acetate and ammonium hydroxide as the electrolytes. The strong alkaline solutions should not stand longer than momentarily in the tin, unprotected by a current, but it is not necessary to have the circuit closed before putting in the reagents. The deposits were gray and very compact. A slight amount of loose material may be brushed out and the dish used for another determination, but if too thick a coating of nickel is deposited it will be found very difficult to remove. The nickel was dissolved with potassium cyanide aided by the current or by nitric acid, specific gravity 1.52.

TABLE XI

$NiSO_4.7H_2O$ = Ni in grams	30 pct. acetic acid in cc.	NH_4OH Sp. Gr. 0.90 in cc.	Volume in cc. when diluted	Approximate temp. at start	Current $N.D_{100}$ = A	Volts	Time in minutes	Ni deposited in gms.	Error in pct. of Ni in $NiSO_4.7H_2O$
0.2500	10	30	100	65°	5	9	13	0.2497	0.03
"	"	"	"	"	"	"	14	0.2502	0.02
"	"	"	"	"	"	"	13	0.2496	0.03
"	"	"	"	"	"	"	"	0.2500	0.00
"	"	"	"	"	"	"	"	0.2504	0.03
"	"	"	"	"	"	"	"	0.2491	0.08
"	"	"	"	"	"	"	"	0.2495	0.04
"	"	"	"	"	"	"	"	0.2501	0.01

Note: Speed of the rotator was about 700 R. P. M.

TABLE XII

$NiSO_4.7H_2O$= Ni in grams	$(NH_4)_2SO_4$ in grams	NH_4OH Sp. Gr. 0.90 in cc.	Volume in cc. when diluted	Approximate temp. at start	Current $N.D_{100}$ = A	Volts	Time in minutes	Ni deposited in grams	Error in pct. of Ni in $NiSO_4.7H_2O$
0.2500	1.5	25	100	65°	5	18-10	15	0.2500	0.00
"	"	"	"	"	"	"	"	0.2497	0.03
"	"	"	"	"	"	"	16	0.2504	0.03
"	"	"	"	"	"	"	15	0.2500	0.00

Note: This series was run by Mr. Hill. Speed of the rotator was about 550 R.P.M.

DEPARTMENT OF CHEMISTRY, SWARTHMORE COLLEGE
May 18, 1907.

THE DETERMINATION OF MANGANESE IN WATER.

BY ROBERT SPURR WESTON.
Received April 20, 1907.

The need for a convenient method of determining manganese in water has been recognized by many analysts. In the ordinary practice of the water analyst either the determination is made gravimetrically or it is omitted.

Manganese together with iron occurs in many ground waters, and very often its presence complicates or vitiates the processes used for the re-

[1] This Journal, 25, 899.

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moval of iron from water supplies. At Breslau, in 1904, the sudden presence of manganese in the ground water made the supply useless for a time, notwithstanding the fact that the water was treated by aeration and filtration for the purpose of removing the iron from it.

Extremely valuable data are missing because of the inconveniences of the present time-consuming methods for the determination of manganese. Such data will be collected only if the methods be as facile as other methods used in water analysis. Waters rarely contain more than 10 milligrams of manganese in a liter. Gravimetric methods are often beyond consideration, and the only ones which seem generally practicable are those in which the manganese is oxidized to permanganic acid. Of these latter the lead oxide methods of Chatard and others[1] and the sodium bismuthate method seemed to be the most promising. The sodium bismuthate method was used because of the greater ease with which the solution could be freed from the precipitate. This method has been used for the determination of manganese in ores and steels and is described by Blair[2]. It was proposed by Schneider[3] and modified first by Reddrop and Ramage[4] and then by Bearley and Ibbotson.[5]

The method is based upon the fact that in the presence of an excess of nitric acid a manganous salt is oxidized to permanganic acid by bismuth tetroxide. Blair states that :—

"The permanganic acid formed is very stable in nitric acid of 1.135 sp. gr. when the solution is cold, but in hot solutions the excess of bismuth tetroxide is rapidly decomposed and then the nitric acid reacts with the permanganic acid and as soon as a small amount of manganous salt is formed the remainder of the permanganic acid is decomposed, manganous nitrate dissolves and manganese dioxide precipitates."

Reddrop and Ramage showed that it was difficult to get bismuth tetroxide free from chlorides, the presence of which would vitiate results, so they proposed the use of sodium bismuthate.

The manganese in the permanganic acid produced by oxidation may be determined in two ways. After filtering off the excess of bismuthate Blair adds an excess of ferrous sulphate to the filtrate and by titration with permanganate solution determines the amount necessary to deoxidize the permanganic acid. For waters containing less than 1 milligram of manganese, however, comparison of the filtrate colorimetrically with permanganate run from a burette into an equal volume of dilute sulphuric acid free from organic matter contained in a Nessler tube, proved to be simpler and more precise ; for larger quantities, however, the titration method should be used.

[1] Sutton's Volumetric Analysis.
[2] This Journal, 26, 793.
[3] Dingler. pol. J., 269, 224.
[4] J. Chem. Soc,, 1895, 268.
[5] The Analysis of Steel Works Materials.

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Method.

Evaporate with about 25 cc. of nitric acid (sp. gr. 1.135) enough of the sample of water to give from 0.01 to 1 mg. of manganese. Gently ignite the residue or bake it for ½ hour at 130°. Add 50 cc. of nitric acid (sp. gr. 1.135) and when the solution is cool add about 0.5 gram of sodium bismuthate. Heat until the pink color disappears.

At this point Blair, in his determination of manganese in iron, adds sulphurous acid, ferrous sulphate or sodium thiosulphate, to clear the solution if manganese dioxide is precipitated, and heats it to dispel all oxides of nitrogen. With waters this step was usually unnecessary, but whenever so, thiosulphate was the reagent used.

To the cool solution add sodium bismuthate in excess, stir a few minutes, and filter through thoroughly washed asbestos in a Gooch filter. Wash with dilute nitric acid, transfer filtrate to a large Nessler tube, and make up to 100 cc. with dilute nitric acid.

In another tube put 100 cc. of dilute sulphuric acid and add standard potassium permanganate solution until the color of the sample is matched. The volume of potassium permanganate in cc. x 0.0001 gives the weight of manganese in grams. Express results as parts per million, —milligrams per liter.

Reagents.

Potassium Permanganate Solution.—Dissolve 0.288 gram of potassium permanganate in water and make up to 1 liter. 1 cc. is equivalent to 0.1 mg. manganese.

Nitric Acid (sp. gr. 1.135). A mixture of 3 parts of water and 1 part of strong nitric acid (sp. gr. 1.42) is used.

Dilute Nitric Acid. 30 cc. of strong nitric acid to the liter.

Sulphuric Acid. 25 cc. of pure concentrated sulphuric acid to the liter. Add enough permanganate to color the solution slightly but perceptibly pink.

Asbestos. Prepare asbestos in the usual way by washing with acid and igniting. It should be free from organic matter.

Notes and Precautions.

The first experiments with this method gave unsatisfactory, erroneous results. Each reagent was tested to ascertain the cause of the error. It was found that the "C.P." nitric acid used was impure; it contained oxides of nitrogen. Several methods of purification were tried. The most efficient process proved to be that of passing a current of air through the concentrated acid for about half an hour

The presence of organic matter also vitiates results; when in large amounts the color of permanganic acid does not appear in the filtrate. This difficulty is overcome by ignition of the residue or by baking it for

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½ hour at 130°. The asbestos must be free from organic matter; otherwise the permanganic acid will be reduced.

The presence of chlorides also interferes with the determination. Samples which contain large amounts of chlorine should be treated before evaporation with a slight excess of silver nitrate and then filtered.

Experiments were made in which the bismuthate was added but once, the excess filtered off immediately, and the permanganic acid determined. Satisfactory results, however, were not obtained by this shorter method. The oxidation is complete only after the second addition of bismuthate.

The method is very delicate. It will detect 0.00002 gram of manganese.

Experiments.

The first experiments were made with distilled water and known solutions of manganese sulphate and potassium permanganate. The results were as follows:—

A. WITH MANGANESE SULPHATE

No.	Grams Manganese Added	Grams Manganese Recovered
1	0.00010	0.00009
2	0.00010	0.00010
3	0.00010	0.00010
4	0.00050	0.00050

B. WITH POTASSIUM PERMANGANATE

No.	Grams Manganese Added	Grams Manganese Recovered
1	0.00010	0.000095
2	0.00020	0.00020
3	0.00050	0.00045

C. Effect of Organic Matter.—Experiments were made like the above, except with the addition of varying volumes of leaf infusion, this being considered typical of the organic matter contained in water. The results were as follows:—

(a) WITHOUT IGNITION OF RESIDUE

No.	Grams of Manganese Added	cc. Leaf Infusion	Grams of Manganese Recovered
1	0.00010	1	0.00010
2	0.00010	2	0.00008
3	0.00010	10	0.00007
4	0.00010	25	Color faded in 5 min.

(b) RESIDUE IGNITED

No.	Grams of Manganese Added	cc. Leaf Infusion	Grams of Manganese Recovered
1	0.00010	25	0.00010
2	0.00010	25	0.00010

D. Two trials of the method were made, first with Boston water, a surface supply, and second with Reading water, a ground water supply containing about 2 parts per million of iron. The Boston water contains no appreciable amount of manganese, but manganese is present in the

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Reading water. Besides determining the manganese in the water, determinations were made with the water containing varying amounts of added manganese.

(a) BOSTON WATER

No.	cc. taken	Grams of Manganese Added	Grams of Manganese Recovered
1	100	0.00000	0.00000
2	100	0.00010	0.00009
3	100	0.00010	0.00010
4	1000	0.00010	0.00009

(b) READING WATER

No.	cc. taken	Grams of Manganese Added	Grams of Manganese Recovered
1	100	0.00000	0.000065
2	100	0.00000	0.000070
3	100	0.00000	0.000075
4	100	0.00010	0.000170
5	100	0.00010	0.000170
6	100	0.00010	0.000165

E. The following experiment shows the effect upon the determination of large amounts of chlorine.

No.	cc. Boston City Water	mgs. Chlorine added to a liter	Grams Manganese Added	Grams Manganese Recovered
1	1000	50	0.00010	0.000085
2	1000	500	0.00010	0.000075
3	100	50	0.00010	0.000079
4	100	500	0.00010	0.000080
5	100[1]	500	0.00010	0.000080

The writer finds this method rapid, convenient, serviceable, and reasonably accurate. He recommends it to other analysts with the hope that more data regarding the manganese content of ground waters may be placed on record.

He also wishes to thank his friend, Professor Henry Fay, for fundamental suggestions, and to acknowledge the services of his assistant, Miss Grace Ide Fairchild, who has made most of the determinations.

14 BEACON ST., BOSTON, April 15, 1907.

A RAPID METHOD FOR THE DETERMINATION OF CALCIUM IN WATER, AND ITS SIGNIFICANCE IN CONNECTION WITH THE ANALYSIS OF WATER FOR BOILER PURPOSES.

BY F. E. HALE.

Received May 17, 1907.

In the examination of water for boiler purposes it is extremely important to be able to determine the relative amounts of calcium and magnesium salts present. The determination of the total hardness by the

[1] Boston water contains about 2.5 parts of chlorine per million.

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soap method furnishes a rapid and fairly accurate means of finding the total calcium and magnesium content. With the development of a rapid and accurate method of determining the total calcium there is at hand the means of knowing the total magnesium, since the latter is the difference between the total hardness and the total calcium. Again the determination of the alkalinity by titration with N/50 sulphuric acid in the presence of methyl orange as an indicator gives us a rapid and accurate means of ascertaining the amount of carbonates. By these three methods combined the characteristics of a boiler water become at once apparent.

The method[1] here described is an adaptation to water of an old and standard method for calcium. The results are very accurate and a complete analysis may be made in thirty minutes. The order of procedure is as follows:

Method of Determination. To 100 cc. of the water to be examined add 10 cc. of a saturated solution of ammonium chloride and 1 cc. of ammonium hydroxide (1 : 1). Precipitate the calcium by adding oxalic acid in solution (5 cc. of a saturated solution made from the recrystallized acid) until a faintly acid reaction is obtained, as determined by a few drops of azolitmin solution or by the absence of the odor of ammonia. Any iron or aluminum precipitated by the ammonia will redissolve. It is better to add one-half of the oxalic acid first and rotate vigorously before bringing to acid reaction. Add an excess of ammonium oxalate (5 cc. of a saturated solution), boil vigorously for fifteen minutes and filter on asbestos in a platinum Gooch crucible, previously ignited, but not weighed. Wash the beaker four or five times with hot water beginning at the top and covering every portion of the sides of the beaker to the bottom, decanting into the crucible each time. Wash the crucible down once or twice, remove and wash down the outside. The total wash water is usually between 35 cc. and 50 cc. Do not clean the beaker with a policeman but place the crucible in the beaker. Add boiling water sufficient in amount to cover the crucible, pour 10 cc. of sulphuric acid (1-1) into the liquid and titrate the oxalic acid of the precipitate with N/50 permangate. From the total number of cubic centimeters of permangate used substract 0.3 cc. for a blank and each 0.1 cc. remaining equals one part per million of calcium, calculated as calcium carbonate.

The above strength of permanganate is the proper strength to use for 100 cc. of water up to 500 parts per million of calcium calculated as calcium carbonate. For quantities of calcium above that amount the quantity of water taken for analysis should be reduced to 50 cc., or other convenient volume, and diluted with distilled water. For

[1] Sutton, Volumetric Analysis, page 161; Peters, Am. Jour. Sci., Vol. X, page 362.

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quantities of calcium below 20 parts per million it is advisable to use 200 cc. of the water to be analyzed.

Complete precipitation of the calcium may also be obtained by heating on a steam bath, but requires one to two hours. This manner of heating does not lengthen the time of attention required from the chemist, which in any case is but 10-15 minutes, and is preferable in routine work. The bath used by the author was of such construction that the beakers rested on the top of an inside drying oven and were surrounded by live steam.

So many chemists experience difficulty in using a Gooch crucible that it may be well to mention the simple manner in which the asbestos is prepared. Long fiber asbestos[1] is pulled apart into shorter lengths, about one-half inch, and each clump gently squeezed together from the ends to separate the fibers, which are then vigorously shaken out in distilled water in a stoppered Erlenmeyer flask. No further preparation, such as washing with acid, is needed. This material furnishes a silky mat which allows of rapid filtration and retains the finest precipitate. A single filtration is usually sufficient, although the filtrate should always be carefully watched and occasionally it is necessary to pass the liquid through a second time. In preparing an asbestos felt suction should be released gradually to avoid injuring the continuity of the felt, and in igniting it care should be taken that the crucible be fanned with the flame until it is dry, to avoid blowing any fine holes in the felt by steam.

Examination of the Method.

The solutions employed were as follows:

Calcium chloride solutions, carefully standardized gravimetrically.

Aluminum sulphate solution, neutral.

Ferric sulphate solution, slightly acid, containing ammonium chloride and nitrate.

Magnesium sulphate solution.

N/100 permanganate solution, made from the N/10 solution and carefully standardized against N/10 oxalic acid.

In testing the accuracy of this method under all possible conditions several hundred experiments have been made including more than a hundred analyses of natural waters. The examples given in the accompanying table will suffice to show the accuracy of the results under extreme artificial conditions. Purposely absurd conditions were chosen in the first two experiments, and, since such amounts of aluminum and iron do not interfere, smaller amounts certainly will not. Corroborative experiments have shown this to be true. Magnesium in large amounts does not interfere even with small amounts of calcium when precipitated as described in this article. Simple precipitation by ammonium oxalate in

[1] Procured from Eimer & Amend, N. Y. City.

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neutral solution has been shown by experiment to be incomplete with small amounts of calcium in the presence of large amounts of magnesium[1], hence the adoption of the above method of precipitation. A good excess of ammonium oxalate is necessary to the success of this method and much excess of oxalic acid is to be avoided. Washing the precipitate of calcium oxalate with hot or with cold water, or with hot ammonium chloride solution produces no difference in the results. Soluble organic matter, such as produces color in water, is without effect. Insoluble organic matter will produce a slight affect; for example, microscopic organisms in very large amounts (10,000 to 25,000 units per cubic centimeter) may produce an error of a few parts per million, but, in such rare instances, or in case of sewage analysis, the sample should be filtered before precipitation of the calcium. It is essential to recrystallize the oxalic acid, as it was found that grave errors may arise from failure to do so. Several parts per million of calcium may be precipitated from impure oxalic acid, which in saturated solution readily holds calcium in solution.

It has been stated by Richards, McCaffrey and Bisbee[2] that one liter of water at 95° dissolves 14 mgrms. of calcium oxalate and at 25° dissolves 6.8 mgrms. The amount of wash water used in the analysis is approximately 30 cc. Consequently, when using boiling water in washing, there should result an absolute error of about 3.5 parts per million of calcium carbonate, and, when using cold water, of about 1.5 parts per million. No such negative error has appeared as a constant in this work. It appears that, while many substances may exert a slight effect in preventing complete precipitation of calcium, the oxalate once precipitated in proper crystalline condition does not readily redissolve.

This method for calcium has been tried and used very successfully by a fellow chemist. The following is an interesting proof of its accuracy. One liter of a mineral water was evaporated and the calcium determined in the usual way to be 117 parts per million. The method of this paper gave 118 parts per million. There were also present 119 parts of magnesium calculated as calcium carbonate.

Calculation and Interpretation of Mineral Analyses.

Various schemes are followed in combining the elements present in a water into salts. Almost all of them follow, more or less, the solubility of the salts, beginning with sodium chloride and ending with the carbonates. On account of the difficulty of obtaining proper figures for sodium and potassium, and the ease with which the carbonates, sulphates, chlorides, calcium and magnesium may be determined, as well as the fact that it is these latter salts which concern us in the question as to whether a water is good or bad for boiler use, it would seem far more advantageous to com-

[1] Fresenius, Quant. Chem. Anal., p 73, c., page 145.
[2] Proc. Am. Acad., 36, 377-393.

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bine the elements according to the degree of insolubility of their salts, beginning with the carbonates and sulphates and ending with the nitrates

Number of Experiment	Quantity of water Analyzed	Ammonium chloride (saturated solution)	Ammonium oxalate (saturated solution)	Ammonium hydroxide (solution 1:1)	Oxalic acid (saturated solution)	Azolitmin used as indicator	Heated on steam bath	Aluminum	Ferric iron	Magnesium sulphate, calculated as $CaCO_3$	Calcium chloride introduced, calculated as $CaCO_3$	Calcium found, calculated as $CaCO_3$	N/100 Permanganate solution required
	cc.	cc.	cc.	cc.	cc.		hrs.	(In parts per million.)					cc.
1	100	10	10	moderate	(+)	(—)	3	100	100	...	248	249.0	49.8
2	"	"	"	"	"	"	2	100	100	...	24.8	24.5	4.9
3	"	"	"	"	"	(+)	3	...	...	...	140	140.0	28.0
4	"	"	"	5	"	"	1.5	...	...	...	140	140.0	28.0
5	"	"	"	"	"	"	1	...	...	...	140	141.5	28.3
6	"	"	"	"	"	"	1.5	...	...	100	140	140.5	28.1
7	"	"	"	"	25	"	2	...	...	100	140	141.0	28.2
8	"	"	"	"	(+)	"	1.5	...	...	100	70	70.5	14.1
9	"	"	"	"	25	"	2	...	...	100	70	71.0	14.2
10	"	"	"	"	"	(—)	"	...	...	100	35	37.5	7.5
11	"	"	"	"	"	(+)	"	...	...	100	35	37.5	7.5
12	200	"	"	"	(+)	"	1.5	...	...	100	7	8.0	3.2
13	"	"	"	"	25	(—)	2	...	...	100	7	7.0	2.8
14	"	"	"	"	"	"	"	...	...	100	3.5	2.3	0.9
15	100	"	"	"	"	"	"	...	...	100	0	0.0	0.0
16	"	"	5	1	5	(+)	"	...	...	100	280	280.0	56.0
17	"	"	"	"	"	"	"	...	...	100	140	140.0	28.0
18	"	"	"	"	"	"	"	...	...	100	70	71.0	14.2
19	"	"	"	"	"	"	"	...	...	100	35	37.0	7.4
20	200	"	"	"	"	"	"	...	...	100	7	7.0	2.8
21	"	"	"	"	"	"	"	...	...	100	3.5	1.8	0.7

(+) and (—) mean that the solutions heading the column were or were not used.

and chlorides. We have, then, sufficient data at hand for a judgment, whether we have a complete analysis or not. Furthermore, it is best to combine according to the solubilities at ordinary temperatures, because little is known with certainty as to what changes take place under the different conditions in the boiler. Cecil H. Cribb[1] has published a very instructive article on the Influence of Temperature and of Concentration on the Saline Constituents of Boiler Water. Proper reactions, as these are determined, may be written from the combinations at ordinary temperatures to show what will happen in the boiler at high temperatures and pressures. For example, at boiling temperature solutions of magnesium sulphate and calcium carbonate react to form basic magnesium carbonate and calcium sulphate with loss of carbon dioxide, and in the boiler this

[1] Analyst, July, 1900, p. 169.

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basic carbonate undoubtedly is deposited practically as the oxide, or hydroxide of magnesium, allowing the free carbon dioxide to act corrosively upon the boiler. In this reaction there are two insoluble bodies to help along the reaction, calcium sulphate and magnesium oxide. There is no reason to doubt that magnesium chloride and calcium carbonate under like conditions would react to form calcium chloride and the very insoluble magnesium oxide with loss of carbon dioxide.

Not much deposition of hard scale can take place in a boiler until considerable concentration has been reached, unless the water is very hard, since calcium sulphate is soluble to the extent of 270 parts per million at a pressure of 132 pounds per square inch, and to 180 parts at a pressure of 513.5 pounds per square inch[1].

To return to the insolubility at ordinary temperatures of the salts under consideration. Watt's Chemical Dictionary furnishes the following data:

	Grams dissolved in 100 grms. of water.	Parts per million.	Temperature.
Calcium sulphate,	0.19	1,900	0° C.
	0.206	2,060	20° C.
	0.214	2,140	40° C.
Calcium carbonate neutral,	0.0094	94	cold.
Calcium carbonate, in water saturated with carbon dioxide,	0.07	700	0° C.
	0.088	880	10° C.

From this table it is seen that, even in the presence of carbon dioxide, calcium carbonate, at ordinary temperatures is more insoluble than calcium sulphate.

Again, C. H. Bothamley[2] found that solid calcium carbonate in contact with magnesium sulphate solution, or solid magnesium carbonate in contact with a solution of calcium sulphate, resulted always in a solution of magnesium sulphate and a deposit of calcium carbonate. Hence calcium carbonate is more insoluble than magnesium carbonate. The sulphate of magnesium is, of course, very soluble, as are the chlorides and nitrates of calcium and magnesium.

The procedure would then be to calculate the alkalinity to calcium first, unless the alkalinity exceeds the total hardness, which rarely occurs, and then only when carbonates of sodium and of potassium are present. If the carbonates exceed the necessary amount of calcium, the rest of the alkalinity may be calculated to magnesium carbonate, and sulphates, chlorides, etc., combined with magnesium until the latter is exhausted. But if the calcium exceed the amount necessary to take care of the alkalinity, there is no magnesium carbonate, and the excess of calcium may then be calculated to sulphate first, then chloride or nitrate until exhausted, and the magnesium is combined with the remaining acid radi-

[1] Tilden and Shenstone, Phil. Trans., part 1, 1884, p. 23.

[2] J. Chem. Soc., 1893, 698.

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cals until exhausted. Any remaining chloride, nitrate, and sulphate may be calculated to sodium and potassium salts.

Many analyses of mineral waters have been made in which this method for calcium has been profitably employed. Among them are the following:

1. A well-known mineral water gave a hardness of 162 by the soap method and an alkalinity of 160. The total calcium was found by this method to be 155. The magnesium was precipitated in the filtrate from the calcium oxalate and found to be 3 parts per million,—all results expressed, as usual, in terms of calcium carbonate.

2. A water from North Carolina contained the following:

$SiO_2 = 0$, Fe = 3, Total hardness = 1363, Alkalinity = 260, Cl = 8,200, $SO_3 = 250$, N as nitrate = 0. The total calcium, determined by this method, was 483. The magnesium, precipitated in the filtrate, was found to be equivalent to 872 of calcium carbonate. The total calcium and magnesium was then 1355, as against a hardness of 1363. The hardness was determined in 2 cc. portions diluted to 50 cc. with distilled water. Four determinations required 4.7, 4.4, 4.6, 4.6 cc. of soap solution, an average of 4.6 cc. A difference of one quarter of a tenth of a cubic centimeter would account for the discrepancy in the hardness.

Let us examine into the nature of the salts present. The alkalinity all belongs to the calcium, since the total calcium exceeds it. There was then *260* parts per million of *calcium carbonate*. The total calcium less the alkalinity (483—260=223) equals the calcium present in some other form and calculated to sulphate equals *303* parts *calcium sulphate*. Of the SO_3 125 parts are therefor combined with calcium. The total SO_3 250 minus 125 leaves 125 parts SO_3 to be calculated to magnesium sulphate and equals *188* parts *magnesium sulphate*. Of this 63 parts are magnesium oxide and equals 157 in terms of calcium carbonate. The hardness less the total calcium gives the total magnesium in terms of calcium carbonate (1363—483=880). But as the magnesium was actually determined by gravimetric analysis to be equivalent to 872 of calcium carbonate, we will use that figure. The total magnesium minus that in the form of sulphate (872—157=715) equals the amount of magnesium to be calculated to chloride, since the chlorine will more than cover it, and equals *679* parts *magnesium chloride*. Of this 508 parts are chlorine. The total chlorine less that in the form of magnesium chloride is calculated to sodium chloride (8,200—508=7,692) and equals *12,747* parts *sodium chloride*. The result is:

$CaCO_3$ 260, $CaSO_4$ 303, $MgSO_4$ 188, $MgCl_2$ 679, NaCl 12,747.

The sulphate in this analysis was determined by precipitation with barium chloride and Jackson's[1] turbidimetric method, using the candle

[1] This Journal, 23, 801.

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turbidimeter. Hence the complete mineral analysis was accomplished by rapid methods.

3. A well water from Western New York.

Data. Hardness 485, Alkalinity 186, Cl 48, SO_3 213, N as nitrate 7.5. Fixed solids 682. Total calcium 348. Hence total magnesium is equivalent to 137 of calcium carbonate, (485-348).

Calculating in practically the same manner as before, as it happens, we arrive at the result:

$CaCO_3$ 186, $CaSO_4$ 224, $MgSO_4$ 125, $Mg(NO_3)_2$ 39, NaCl 80, SiO_2 and Al_2O_3 28 (by difference).

Conclusion.

In resumé it may be said that the method is admirably suited for the routine analysis of large numbers of samples, may be considered accurate to two parts per million, is applicable to all quantities of calcium including that of sea water, is equally accurate with large and small quantities of calcium, furnishes, in combination with the soap method, a rapid method of determining the total magnesium, and hence is extremely valuable in the rapid analysis of mineral and boiler waters.

MT. PROSPECT LABORATORY,
DEPT. WATER SUPPLY, GAS AND
ELECTRICITY, N.Y. City, Dec. 27, '06.

THE RECOVERY OF ALBUMINOID AMMONIA FROM DISTILLATES CONTAMINATED WITH PERMANGANATE.

BY F. E. HALE.

Received May 22, 1907.

In the distillation of albuminoid ammonia in sanitary water analysis it frequently happens that bumping occurs and permanganate is washed over into the distillate. Usually this happens with a hard water, or is occasioned by the use of alkaline permanganate the alkali of which contains considerable carbonate. Consequently it may usually be prevented by care in selecting for the permanganate solution only alkali containing less than five percent of carbonate and by taking care in the preparation of the alkaline permanganate solution to pour it into the retaining bottle as soon as sufficiently cool after boiling off the ammonia. The easiest remedy, when bumping has occurred, is to distill a second portion of the water which is being analyzed, but occasionally this is impossible from lack of sufficient water and a method of recovery from the distillate seems to be worthy of description.

The method, which is entirely of a chemical nature, consists in reducing the permanganate by an alkaline sulphite solution, oxidizing the manganous salt to the hydrated peroxide, filtering off the manganese on

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a carefully washed filter paper, nesslerizing the filtrate, and reading in the usual manner.

The alkaline sulphite solution contains 350 grms. potassium hydroxide to the liter, free from ammonia, and may be so made by boiling. It also contains 30 grms. sodium sulphite, $Na_2SO_3.7H_2O$, as determined by titration with permanganate. The sulphite was found to be free from ammonia and for that reason, as well as for its reaction with permanganate in the cold, it was chosen instead of oxalic acid.

Hydrogen peroxide was tried in the reoxidation of the manganese but failed to meet the requirements of the process, and the simplest and best way was found to be merely leaving the solution exposed to the air over night, at least for several hours, until the manganese was completely reoxidized, as shown by the appearance of the brown precipitate and the absence of any green color in the solution.

Schleicher and Schüll's 12 cm. folded filters No. 588 were found to be more readily washed free from ammonia than ashless filters.

Two things are essential to the process. Every trace of manganese must be removed from the distillate, as it gives a color with Nessler solution comparable with that of ammonia. Not a trace of ammonia must be introduced or removed from the distillate. The method in detail is as follows:

To the distillate add 1 cc. of the alkaline sulphite solution, rotate, and allow to stand over night exposed to the air. Freshly wash a Schleicher and Schüll small folded filter until free from ammonia. This requires 50 to 100 cc. of redistilled water. The filter should be washed just before using, as a wet filter takes up ammonia from the air quite rapidly. Filter off the manganese hydrated peroxide and pour the filtrate through a second time into a fresh tube. Wash the tubes and filter paper with a very little redistilled water (not over 10 cc. is necessary), nesslerize and read. The wash water must necessarily be quite free from ammonia.

The theoretical and practical tests of the process have been very satisfactory. A solution of ammonium chloride was made up of standard strength; that is, each cubic centimeter contained 0.01 mgrm. of nitrogen. Of this solution varying quantities were taken, 1 cc., 2 cc., 3 cc., 5 cc., 8 cc., 10 cc., and 20 cc., and diluted to 50 cc., in nessler tubes. To one set was added alkaline permanganate to a strong coloration and then the permanganate was removed by the method described and the ammonia determined. These values were compared with those obtained by direct nesslerization of a second set without permanganate, all comparisons being made with a set of permanent standards. The following table gives the average of several sets of results:

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Ammonium chloride Solution taken. cc.	Theoretical Value. mgrm. N.	Determination in blank mgrm. N.	Treated solution. mgrm. N.
1	0.010	0.010	0.010
2	0.020	0.017	0.016
3	0.030	0.027	0.030
5	0.050	0.046	0.049
8	0.080	0.081	0.077
10	0.100	0.095	0.095
20	0.200	0.206	0.198

The following are a series of results, extending over several years, obtained from distillates into which permanganate had been washed because of bumping. The original sulphite solution has kept well and has been in use during this time. The figures in parentheses were recovered by this process. The results are expressed in decimal parts of 0.01 mgrm.

Tube.	1	2	3	4	5	6	7	8	9	10
1st.	0.5	2.6	1.4	1.1	2.8	2.5	2.4	1.7	1.9	1.9
2nd,	0.3	0.8	0.7	0.6	(1.2)	(1.1)	1.3	0.9	(0.9)	(0.9)
3rd.	0.2	0.6	0.4	0.4	0.6	(0.7)	0.8	(0.7)	(0.6)	(0.4)
4th.	0.2	(0.4)	0.2	0.2	0.5	(0.6)	(0.6)	(0.3)	(0.4)	(0.3)
5th.	(0.2)	0.4	(0.1)	(0.1)	0.4	0.4	0.5	0.2	0.4	0.2

	11	12	13 U.	13 F.	14 U.	14 F.	15 R.	15
1st.	2.4	2.1	2.3	1.5	1.6	1.2	1.8	(1.7)
2nd.	(1.2)	1.0	0.9	(0.5)	0.8	(0.7)	0.8	(0.8)
3rd.	0.8	0.7	0.6	(0.4)	(0.5)	0.5	0.5	(0.5)
4th.	0.5	(0.3)	0.4	0.4	(0.3)	0.4	0.4	
5th.	(0.4)	0.3	0.3	0.3	0.3	0.3	0.3	

	16		17	
	Free Ammonia.	Alb. Ammonia.	Free Ammonia.	Alb. Ammonia
1st.	(0.6)	(3.2)	(1.4)	(3.6)
2nd.	(0.1)	(1.2)	(0.6)	1.3
3rd.	(0.0)	0.8	(0.1)	1.1
4th.		0.4		0.4
5th		0.2		0.3

Analyses No. 13 and No. 14 give a comparison between figures obtained from unfiltered and filtered water. Analysis No. 15 is interesting because it compares figures obtained by repeating the distillation with recovered figures. Analyses No. 16 and No. 17 are interesting because they include all the free ammonia and the highest figures of the albuminoid ammonia. The recovery was rendered necessary by the breaking of a distilling flask and the deluging of the tubes with permanganate.

MT. PROSPECT LABORATORY,
Dept. Water Supply, Gas and
Electricity, May 17 th, 1907.

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THE SOLUBILITY OF ACETANILIDE, PHENACETINE, CAFFEINE AND SALOL IN SEVERAL SOLVENTS.

BY ATHERTON SEIDELL.

Received May, 2, 1907.

The experiments described in this paper were undertaken for the purpose of obtaining the necessary data upon which to base a satisfactory method for the separation of some of the constituents of headache powders. The object was to find solvents in which the solubility of one or more of the above named substances differed most from that of the others under the same conditions. The determinations were therefore not made with the care which should be devoted to results submitted primarily as solubility constants, since it was recognized that only wide differences in the actual amounts of the several substances dissolved by a single solvent, could be utilized for the quantitative separation of mixtures of these compounds.

A search of the literature indicated that comparatively few solubility results which could be used for the purpose, were available. The usual reference books upon pharmaceutical and organic chemistry give approximate determinations for each of these substances in the more common solvents such as water, alcohol, ether, chloroform, etc. In addition to data of this character there were found results upon the solubility of acetanilide in methyl alcohol, ethyl alcohol, and chloroform by Speyers[1] and in mixtures of ethyl alcohol and water by Holleman and Antusch.[2]

The material used for the determinations here recorded was in all cases that sold under the designation C. P. or U. S. P. The experiments were made at room temperature and therefore the temperatures recorded are probably accurate in most cases to within a degree or two.

The method of determination was as follows: About 30 cc. of the solvent and an excess of the solid in each case were placed in glass stoppered cylinders which were then attached to an axle which was rotated by means of a water motor. All determinations in any one solvent were made simultaneously and hence are comparable in so far as temperature, time of shaking etc. are concerned. The time of rotation was at least six hours in all cases, usually much longer. The removal of a clear portion of the solution was effected by drawing it up with the aid of suction into a pipette provided with a filter of absorbent cotton at the opening through which the liquid entered. The solution was then transferred to a pycnometer and after being weighed was washed (usually with alcohol) into a tared platinum dish. The solvent was then removed by evaporation at room temperature with the aid of an electric

[1] Speyers, Am. J. Sci. (4), 14, 294, (1902).
[2] Holleman and Antusch, Rec. trav. chim., 13, 293, (1894).

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fan. The residue remaining in the dish was alternately weighed and dried at 60° until no further loss occurred.

In the case of benzaldehyde, the benzoic acid formed during the evaporation was determined by titration with standard alkali and its amount deducted from the total weight of residue found. With salol in benzaldehyde, however, a determination could not be made since no solid separated even on continued evaporation of the solution by means of the current of air.

The first series of determinations were made in aqueous ethyl alcohol solutions and the results are presented in Table I together with those of Holleman and Antusch upon similar aqueous alcoholic solutions, determined at 25°. Eight saturated solutions were prepared and rotated at the temperature of the room which held closely at 30° for several hours previous to the withdrawal of portions for the analysis.

TABLE I.

SOLUBILITY OF ACETANILIDE IN MIXTURES OF ETHYL ALCOHOL AND WATER.

Weight Percent Alcohol in Mixtures	Results at 25°[1]		Results at 30°	
	Gms. $C_6H_5NHOC_2H_3$ per 100 gms Sat. Solution	Sp gr. of Solution	Gms. $C_6H_5NHOC_2H_3$ per 100 gms. Sat. Solution	Sp. gr. of Solution
0	0.54	0.997	0.69	1.000
10	0.93	0.985	1.00	0.984
20	1.28	0.973	2.20	0.970
30	2.30	0.962	4.80	0.956
40	4.85	0.950	9.40	0.945
50	8.87	0.939	15.40	0.934
60	14.17	0.928	22.00	0.926
70	19.84	0.918	27.60	0.917
80	25.17	0.907	31.20	0.907
85	26.93	0.899	31.70	0.900
90	27.65	0.890	31.60	0.893
95	26.82	0.874	30.80	0.885
100	24.77	0.851	29.00	0.876

The weight percents of alcohol in the eight water alcohol mixtures used were calculated from their specific gravities determined by the pycnometer method. The dissolved acetanilide was determined by weighing the residue left after the evaporation of the solvent from weighed portions of the saturated solutions. The interpolated values shown in the table were read from the curve drawn through the eight points plotted on cross section paper. For this curve, the weight percents of alcohol in the alcohol-water mixtures were taken as abscissas and the grams of acetanilide per 100 grams of solution as ordinates. The curve plotted in the same manner from the 25° results of Holleman and Antusch lies somewhat below the 30° curve but in all other respects the two are entirely similar. An examination of these curves shows that the amount of dis-

[1]Holleman and Antusch.

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solved acetanilide increases at first slowly with increase in concentration of alcohol, and then quite rapidly up to the maxima, which in the case of the 25° curve is at 90 weight percent alcohol and in the case of the 30° curve is at 85 percent alcohol. Above these concentrations of alcohol the solubility diminishes in each case. A satisfactory explanation for this increased solubility of acetanilide in alcohol containing 10 percent water (and even more at a higher temperature) is at present not apparent.

The solubility of acetanilide in methyl alcohol, ethyl alcohol and in in chloroform as determined by Speyers[1] is reported in terms of gram molecules of acetanilide per 100 gram molecules of the solvents at irregular temperatures, and in addition the weights of the saturated solutions are given for other temperatures than those at which the solubility determinations were made. Although no new results for these solvents have been determined by the present writer it was thought of interest to recalculate those of Speyers to the basis selected for presenting all the other solubility determinations included herewith. This has been done and the results given in Table II,

TABLE II.

SOLUBILITY OF ACETANILIDE IN METHYL ALCOHOL, ETHYL ALCOHOL AND IN CHLOROFORM (SPEYERS).

Temperature.	In Methyl Alcohol		In Ethyl Alcohol		In Chloroform	
	Gms. $C_6H_5NHOC_2H_3$ per 100 gms. Solution	Wt. of 1 cc. Solution	Gms. $C_6H_5NHOC_2H_3$ per 100 gms. Solution	Wt. of 1 cc. Solution	Gms $C_6H_5NHOC_2H_3$ per 100 gms. Solution	Wt. of 1 cc. Solution
0	18.5	0.860	12.8	0.842	3.53	1.503
10	23.1	0.864	16.7	0.844	7.24	1.475
20	29.1	0.875	21.3	0.850	10.7	1.440
30	35.1	0.892	26.5	0.860	14.5	1.398
40	42.9	0.911	32.9	0.874	18.7	1.354
50	51.7	0.932	39.4	0.895	23.7	1.314
60	59.2	0.957	46.4	0.920	29.1	1.272

In Table III is shown the comparative solubilities of acetanilide, phenacetine, caffeine and salol in twelve different solvents. Although this number is not as large as would be desirable in order to fully accomplish the purpose mentioned in the first part of this paper, it is believed that a fair degree of success can be attained in the separation of mixtures of at least three of the above named substances on the basis of the results shown in the table. Thus it may be expected that with proper manipulation either toluene, benzene or xylene will remove salol when mixed with the other three compounds, and amyl alcohol or acetate will effect a separation of caffeine from a mixture of this substance with acetanilide and phenacetine. It is seen that with none of the solvents is there a wide difference between the solubility of acetanilide and phenacetine.

[1] loc. cit.

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TABLE III.

SOLUBILITY OF ACETANILIDE, PHENACETINE, CAFFEINE AND SALOL IN ORGANIC SOLVENTS.

Solvent.	Sp. gr. of solvent.	t°	Grams per 100 grams saturated solution: Acetanilide.	Phenacetine.	Caffeine.	Salol.
[1]Water	0.997	25	0.56	0.11	2.14	insoluble
[1]Ether	0.716	"	7.7	1.56	0.27	———
[1]Chloroform	1.476	"	16.6	4.76	11.0	———
Acetone	0.827	30-31	31.15 (0.902)	10.68	2.18 (0.832)	90.99
Benzene	0.872	"	2.46 (0.875)	0.65 (0.873)	1.22 (0.875)	88.57 (1.148)
Benzaldehyde	1.055	"	18.83 (1.068)	8.44 (1.063)	11.62 (1.087)	?
Amylacetate	0.860	"	10.46 (0.882)	2.42 (0.865)	0.72 (0.862)	85.29 (1.136)
Aniline	1.02	"	19.38 (1.034)	9.46 (1.025)	22.89 (1.080)	very soluble
Amylalcohol	0.814	25	14.00	3.51 (0.819)	0.49 (0.810)	20.44 (0.869)
Acetic acid[2]	1.055	21.5	33.21	13.65 (1.064)	2.44	63.24 (1.143)
Xylene	0.847	32.5	1.65 (0.847)	1.25 (0.847)	1.11 (0.847)	87.14+
Toluene	0.862	25.0	0.50 (0.862)	0.30 (0.863)	0.57 (0.861)	83.62 (1.128)

Figures in parentheses are the specific gravities of the saturated solutions.

Fairly good results have been obtained by the author in separating mixtures of different amounts of salol, caffeine, and acetanilide by digesting first in toluene for the removal of salol and then in amyl alcohol for the removal of the acetanilide.

As is shown by the table, none of the four compounds are completely insoluble in any of the solvents, and consequently it cannot be expected that a very sharp separation can be made. This is especially true for mixtures containing relatively small amounts of either of the substances. It is also to be mentioned that the influence of the presence of one substance upon the solubility of the others in the mixture has not been investigated and therefore conclusions based upon the solubility of single substances in a given solvent may be considerably in error when applied to mixtures of two or more substances acted upon by the same solvent.

The author regrets that circumstances have prevented the extension of these determinations to a larger number of solvents and the application of the results to a more accurate method of separating and determining the constituents of headache powders.

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A RAPID METHOD FOR THE QUANTITATIVE DETERMINATION OF ACETANILIDE IN HEADACHE POWDERS.

BY ATHERTON SEIDELL.

Received May 2, 1902.

While continuing the investigations described in the previous paper a suggestion was obtained which has led to the following method for deter-

[1] Results from U. S. P., 8th Revision.

[2] 99.5 %

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mining acetanilide in presence of many of the substances usually associated with it in the headache and neuralgia remedies found on the market.

In studying the distribution of phenol and of aniline between water and several immiscible solvents Vaubel[1] and subsequently Riedel[2] titrated the phenol or aniline as the case might be with a standard solution of potassium bromate and found that very satisfactory determinations could be made. The method is based upon the well known property of phenol and of aniline to unite with bromine in a strongly acid aqueous solution to form the insoluble tri-bromide in each case. When the precipitation is complete the free bromine in solution is easily detected by the yellow color which it imparts to the liquid. A method based upon this same reaction is given for carbolic acid in the 1890 U. S. Pharmacopœia, page 10. According to this method, however, the excess of added bromate solution (Koppeschaar's solution) is titrated back with standard sodium thiosulphate.

In view of the ready saponification of acetanilide in acid as well as alkaline solutions it was thought desirable to test the applicability of the above method to the determination of the aniline set free from acetanilide by saponification in strongly acid solutions. The preliminary experiments proved entirely satisfactory and it only remained to determine the limits of accuracy which could be attained and ascertain the influence exerted by other substances in solution.

The standard potassium bromate solution may be conveniently prepared by adding bromine to a cold almost saturated aqueous solution of about one hundred grams of potassium hydroxide, until no more is taken up, diluting somewhat with water and heating to expel the excess of bromine, filtering and bringing to a volume of about two liters. The solution may be standardized with weighed amounts of either pure aniline or acetanilide. In the latter case the acetanilide is first boiled several minutes in a moderately concentrated solution of hydrochloric acid and the hot solution titrated. The bromate solution is diluted so that each cubic centimeter corresponds to 0.01 gram of acetanilide; this being a convenient strength to use; although a more dilute standard solution may be used if desired.

Experiments made for the purpose of ascertaining the limits of strength of acid and time of heating necessary for complete saponification of acetanilide showed that the acid solution should contain not less than approximately 1 part of concentrated hydrochloric acid to 4 parts of water and the heating should be continued for at least an hour on the steam bath or the solution boiled energetically for five minutes. In these

[1] J. pr. Chem., (2) **67**, 476, (1903).
[2] Z. physik. Chem., **56**, 243, (1906).

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experiments half gram samples of acetanilide and approximately 60 cc. of the acid solution were used, and the mixtures heated in 200 cc. Erlenmeyer flasks.

In regard to the accuracy which may be attained it was found that with half gram samples of acetanilide, the amounts recovered as calculated from the cc. of standard bromate used agree in practically all cases to within one per cent. of the weight of acetanilide taken.

The next point investigated was the effect upon the reaction of other substances in solution. Among the first of these considered was caffeine. It was found that with half gram samples of acetanilide amounts of caffeine varying between one-half and two grams did not interfere at all with the accuracy of the titration. It is very probable that the presence of caffeine in even larger relative amounts would not seriously affect the accuracy of the determinations although it was noticed that with the larger amounts of caffeine there is some tendency for the yellow color of the free bromine in the solution at the end of the titration to fade on standing.

As is of course to be expected, sodium bicarbonate and other unoxidizable inorganic salts which may possibly be used in headache powders do not interfere with the accurate titration of the acetanilide.

With sugar, which is a frequent constituent of this class of medicines it is found that heating to the temperature of the steam bath or boiling with hydrochloric acid of the concentration required for the saponification of the acetanilide, causes the sugar to carbonize with a resulting darkening of the solution. The dark color prevents the detection of the end point of the reaction, but it is found that in such cases on cooling the solution and adding a little animal charcoal and filtering, the dark color may be satisfactorily removed and an accurate titration of the clear solution made. A more satisfactory plan, however, is to remove the acetanilide from the sample by means of chloroform or some other solvent, and after evaporating the latter, determine the acetanilide as above outlined. In some cases, on the other hand, it may be desirable to dissolve out the sugar and other water soluble constituents with the least possible amount of cold water and then saponify the undissolved acetanilide with hydrochloric acid as described.

Experiments made with mixtures of salol and acetanilide showed that the accuracy of the determination is in no wise influenced by the presence of the salol.

The above named substances are the ones which are usually found in the ordinary headache and neuralgia preparations which are sold by druggists and therefore the very simple and rapid method here described is applicable in the large majority of cases. In order to test the method, a number of headache powders containing various amounts of acetanilide

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mixed with sugar, sodium bicarbonate, caffeine, salol, etc., were prepared and the acetanilide determined by the titration as above described. In all cases the amounts found agreed within a few tenths of a per cent. with the amount which the sample was known to contain.

In addition to acetanilide, the only other substances which have found extensive application in the relief of headaches are phenacetine and antipyrine but the use of these as compared with acetanilide has until recently been largely restricted on account of their higher price. The action of these substances upon the nerve centers is very similar to that of acetanilide and for this reason it is not to be expected that they will generally be used together with acetanilide in headache remedies, nevertheless it was thought desirable to examine their influence upon the titration method described above. A few tests immediately indicated the impossibility of titrating the saponified acetanilide solution with potassium bromate when even the smallest amount of either phenacetine or antipyrine is present in the original sample. In the case of phenacetine the first few drops of the bromate solution turns the liquid pink to purple color and this becomes darker, even to deep black with continued addition of the bromate solution.[1] With the presence of antipyrine the end point of the titration is also obscured.

At the present time apparently the only satisfactory methods available for the quantitative determination of phenacetine and of antipyrine are the Zeisel [2] ethoxy and methoxy distillation method for the former and Bougault's [3] iodine titration method for the latter. A number of determinations made by the author with the Zeisel method indicated that the procedure can be carried out only by a skilled worker, and this fact together with the amount of time required for each determination will undoubtedly impair the usefulness of the method for ordinary practice in control laboratories. In regard to the method for antipyrine, it is evident that the determination can not be made upon samples containing caffeine or other substances which unite readily with free iodine. In view of these considerations it appeared especially desirable to modify the titration method for acetanilide proposed in the first part of this paper, in such a manner that at least quantitative determinations of this substance in presence of phenacetine could be satisfactorily made. With this idea in mind a very large number of experiments have been made and so far only partial success has been attained. The cause of the difficulty lies in the presence of

[1] This observation suggests a simple test for detecting the presence of phenacetine in acetanilide. Dissolve the sample in moderately strong hydrochloric acid, boil and add a few drops of potassium bromate solution, a purple color indicates the presence of phenacetine.

[2] See Tingle's translation of Hans Meyers' little book upon the "Determination of Radicals in Carbon Compounds," p. 38.

[3] J. pharm. chim., (6) 7, 161, 11, 97.

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the ethoxy group in the phenacetine. The bromine acting upon this portion of the molecule converts the compound into an intensely colored quinone derivative which makes it impossible to observe the end point of the reaction. Among the plans for getting around this difficulty which have so far been tried without success may be mentioned, the attempts to remove or render the ethoxy group inactive either by oxidation or reduction methods; titration with the use of spotting plates or test papers upon removed portions of the solution; and the use of mild saponifying agents for liberating aniline from the acetanilide without acting upon the phenacetine.

It was found that although acetanilide alone, and with less success phenacetine, could be titrated directly (without previous saponification) in the cold, acidified, aqueous solution with standard potassium bromate, the reaction is slow since time must be allowed for the dissolving of the phenacetine or acetanilide during the titration, and in addition the presence of caffeine seriously interferes with the determination of the end point.

The only process which has appeared to be worthy of further study is based upon the statements found in Meyer and Jacobsen, vol. 2, p. 455, that chloride of lime acting upon *p*-aminophenols produces quinone chloramide and this product is very easily reduced back to the *p*-phenol by means of reducing agents. Quantitative experiments made with stannous chloride as the reducing agent showed that if an excess of the bromate solution be added to the acid saponified solution of a mixture of acetanilide and phenacetine, this excess could be titrated back with stannous chloride and the difference corresponds fairly closely to the amount required by the acetanilide alone in the mixture. Further work will be required however to demonstrate the practical applicability of this procedure; and in the mean time it is hoped that the method as described for acetanilide alone will prove useful particularly to the chemists having charge of the enforcement of the new Pure Food and Drug Law.

A STUDY OF THE INFLUENCE OF MAGNESIUM SULPHATE ON THE GROWTH OF SEEDLINGS.

By Gertrude S. Burlingham.

Received March 29, 1907.

Introduction

This investigation is an outgrowth of a more comprehensive problem in nutrition, the aim of which was to learn the effects of the different mineral nutrients upon the growth of a test plant, from these data to compound a perfect nutrient solution, and then to note the variations in structure and form which might be produced by modifying the composition of this nutrient solution. *Abutilon abutilon* was chosen as the test plant,

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since it had not been used in any similar experimentation and promised to yield readily to water culture treatment. Early in the work, the response of one seedling to an m/1024 solution of magnesium sulphate attracted attention by the amount of its growth and the length of time which it lived. Accordingly, toxic and stimulation points having been established for various other mineral salts, special attention was given to the effects of magnesium sulphate upon the growth of the abutilon seedlings. The results were so interesting that the investigation was carried farther. The data and conclusions which were established form the basis of this paper. The work is being continued along synthetic lines, and the results that may be obtained in our study of the original nutrition problem will be presented in a future paper.

Magnesium salts, in the absence of calcium, are generally considered to be inhibitory to plant growth. Dr. Loew[1] in his "Physiological role of mineral nutrients in plants," and again[2] in "Liming of soils from a physiological standpoint", treats at some length the effects of magnesium salts on plants. As a result of his observations, he says "Plants succumb soon when placed in diluted solutions of magnesium salts and no other . . . in fact, magnesium salts can exercise their nutritive functions only in the presence of a sufficient amount of calcium salts. . . Only the lowest algae and fungi are exceptions". This is in unison with the findings of Wolff, Raumer, Kellerman, May, and others. On the other hand, Duggar observed that magnesium salts were not very toxic to the marine algae, and True and Gies, in their experiments on "The physiological action of some of the heavy metals in mixed solutions,"[3] found that the toxicity of magnesium chloride for lupin seedlings diminished greatly with dilution. They noted the fact that growth of the lupin root was practically equal in an m/2048 magnesium chloride solution to that in the water control, and also that decided *stimulation* of the growth of the root occurred in an m/4096 solution of magnesium chloride, as compared with that in the water control. It has also been demonstrated that a certain amount of magnesium is necessary for the perfect development of the higher plants, and spores will not form in the lower fungi grown in solutions lacking magnesium. Furthermore bacteria, the lower fungi and the lower algae can thrive in the absence of calcium.[4]

Among some of the most interesting investigations of the influence of magnesium compounds on animals, are the recent experiments of Meltzer and Auer. The results of their studies, from first to last, have led them to conclude "that magnesium favors essentially or exclusively in-

[1] Loew: Bull. 45 Bur. Plant Ind. U. S. Dep't. Agri. (1903.)

[2] Loew: Bull. 1 Bur. Plant Ind. U. S. Dep't. Agri. (1901).

[3] True and Gies: Bull. Torrey Bot. Cl. 30, 390-402 (1903). Also Gies and collaborators: Biochemical Researches, 1, Reprint No. 37 (1903).

[4] Loew: Bull. 45 Bur. Plant Ind. U. S. Dep't. Agri. p. 52.

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hibitory processes in the animal body". The following quotation[1] will give a good idea of their hypothesis. "At a certain phase of functional activity the inhibition of a reflex action, or of a sensation within a ganglion cell, is an indispensable factor in the prompt working of these functions, and these inhibitions require as much vital assistance for their development as is required and received by the positive energies of these tissues. The diastolic part in the cycle of a heart beat; the inhibition of the contraction of the inspiratory muscles in the cycle of a respiration; the inhibition of a disturbing activity of any antagonistic muscle; the inhibition of a disturbing concomitant reflex; the inhibition of the activity of one sense during the act of perception of another sense,—in these and in many other instances the suppression, the inhibition of an activity is an indispensable part of a vital function. Is it not possible that the processes of inhibition are essentially facilitated by compounds which contain magnesium?"

Practically all the effects which Meltzer and Auer noted, were brought about by only relatively large doses, and they have not ascertained the effects of minute proportions. Therefore their results are in accord with those of botanists in indicating that magnesium is decidedly inhibitory in its biological effects, especially when present in quantities that are relatively large.

In this connection it may be well to mention the recent investigations of Loeb[2] upon "The rythmical contractions of a jelly fish." He drew the following conclusions as a result of his work: "1. The experiments show that the normal rythmical motions of a jelly fish (*Polyorchis*) will only occur in such solutions as contain magnesium and that the apparently spontaneous character of these rythmical motions depends upon the magnesium contained in sea water. 2. This effect of magnesium can be inhibited by the addition of an equivalent amount of calcium or potassium. 3. The isolated center of Polyorchis, which will not beat in a pure sugar solution or in sea-water, can be caused to beat in both solutions through the addition of a certain amount of calcium chloride, (or strontium chloride or barium chloride) but not by magnesium chloride. Magnesium inhibits the stimulating effect of calcium when magnesium is added in the ratio of at least four times the equivalent of calcium."

It is in consideration of the present interest in the physiological effects of magnesium and in view of the somewhat different theories advanced, that the results of these investigations upon the influence of magnesium sulphate on the growth of seedlings, are presented with the

[1] Meltzer and Auer: Am. J. Physiol., 14, 367, 1905.
[2] Loeb. J.: J. Biol. Chem., 1, 427, 1906.

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hope that they may throw some additional light upon the biological function of magnesium.

Methods.

The results were first established with the abutilon seedlings, representing a type of plant in which little food is stored in the seed, this supply being exhausted before the seedlings were transferred from the sphagnum to the culture solutions. Beakers of 120 cc. capacity were used for the experiments, the seedlings being supported over the mouth of the beaker through holes in paraffined cork, and held in place by cotton plugs so that all roots were immersed in the solution to the same depth. Three seedlings were grown in each culture in any series, and their growth taken at intervals not greater than 48 hours, (for the first 168 hours), the solutions being renewed at the end of 96 hours. For the purpose of measurement the seedlings were removed from the solution and laid upon a chemically clean glass slide which was placed over a flat metric scale. In this way contamination was made impossible. The magnesium solutions were prepared with distilled water and Kahlbaum "K" salts. The results obtained in the first series are indicated in *table* 1.

TABLE I

Series I with abutilon seedlings and magnesium sulphate. Experiment was started Feb. 10, 1906. Average growth given in millimeters.

H. = hypocotyl. R. = root. Pl. = plumule.

Culture	Sec. Rts. appeared	Growth in 168 Hours	Remarks on growth	Death and symptoms
Water	4th day	29.1 { H.23.1 R. 6.	Pl. started Feb. 17	Tops died Feb. 23
$MgSO_4$				
m/128		19.3 { H.19.3 R.	Pl. did not develop	Rts. flaccid Feb. 17
m/256		18.2 { H.17.6 R. .6	Pl. did not develop	Rts. flaccid Feb. 17
m/512		28. { H.26. R. 2.	Pl. did not develop	Rts. flaccid Feb. 17
m/1024		24.9 { H.21.8 R. 3.1	Pl. started Feb. 17	Rts. flaccid Feb. 17
m/2048	4th day	18.3 { H.15.1 R. 3.2	One died Feb. 17	Rts. flaccid Feb. 23
m/4096		21.3 { H.18.5 R. 2.8		Rts. flaccid Mar. 2
m/8192	4th day	30.6 { H.17.7 R.12.3	Healthy Feb. 17	Tops died Mar. 2
m/16384	4th day	49.6 { H.30.8 R.18.8	Pl. started Feb. 16	Tops died Feb. 24

Results.

The action of *m*/128 and *m*/256 magnesium sulphate solutions was so plainly toxic that they were eliminated in subsequent trials. Although the total growth in *m*/8192 was less than in the control, the root growth was the same in both; while the ratio between the average total growth

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in the control and in *m*/16384 was 29 : 49, and the relation between the root growths was 6:18. In the next series the dilution was carried two points farther. The details of this experiment are given in *table* 2.

TABLE 2

Series 2 with abutilon seedlings and magnesium sulphate. Experiment was started Feb. 26, 1906. Average growth given in millimeters.

H. = hypocotyl. R. = root. Pl. = plumule.

Culture	Sec. Rts. appeared	Growth in 168 hours	Remarks on growth	Death and symptoms
Water	4th day	37.2 { H.27.6 R. 9.6	Pl. started Mar. 13	Tops died 8th day
$MgSO_4$				
m/512		18.4 { H.17.6 R. .8	Pl. did not develop	Roots flaccid 3rd day
m/1024		19.3 { H.18.5 R. .75	Pl. did not develop	Roots flaccid 3rd day
m/2048	4th day	25.1 { H.22.3 R. 2.8	Pl. did not develop	Roots flaccid 8th day
m/4096		27.3 { H.24. R. 3.3	Alive Mar. 7	
m/8192	4th day	61.6 { H.33.3 R.28.3	Pl. started Mar. 5	Tops died 8th day
m/16384	4th day	52.1 { H.38.5 R.13.6		Cotyls dying 8th day
m/32768	4th day	51.6 { H.34.3 R.17.3	Pl. started Mar. 3	See note[1]
m/65536	4th day	71.3 { H.35. R.36.3	Pl. started Mar. 7	Cotyls dying Mar. 13

As a result of the observations recorded in *tables* 1 and 2, it is evident that magnesium sulphate in concentrations greater than *m*/8192 is toxic to seedlings of abutilon, as is shown by the inhibition of growth and the flaccidity of the roots after a few days. While in dilutions greater than this, there are indications of a beneficial action. Accordingly, in the remaining series with abutilon seedlings, *m*/8193 was taken as the starting point.

TABLE 3

Series 3 with abutilon seedlings and magnesium sulphate. Experiment was started Mar. 4, 1906. Average growth for first 168 hours given in millimeters.

H. = hypocotyl. R. = root.

Culture	Growth in 168 hours	Remarks on growth
Water	32.5 { H.28. R. 4.5	Secondary roots numerous in
$MgSO_4$		
m/8192	43.2 { H.27.6 R.15.6	all. Longest in *m*/65536. Plumule
m/16384	53.6 { H.32.1 R.21.5	started first in *m*/16384.
m/32768	44.9 { H.28.6 R.16.3	Condition in all normal, March
m/65536	46. { H.30. R.16.	11

[1] Number 1 died on the 14th day, number 2 lived until June 1, and developed several sets of leaves. The death of number 3 was not recorded but it outlived number 1.

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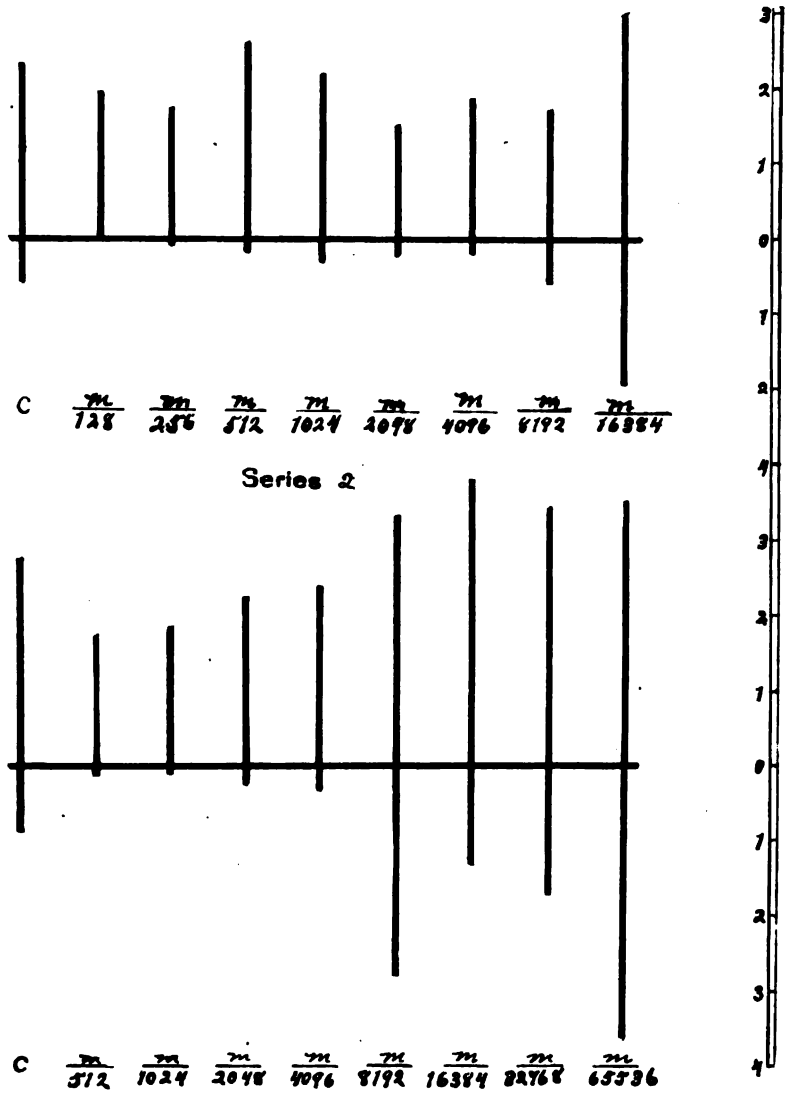


PLATE I

Diagrams showing the actual growth of the abutilon seedlings in the control (*C*) and in the different concentrations of $MgSO_4$ in series 1 and 2.

The marginal units are in centimeters. The root growth is shown below the base line, the growth of hypocotyl, above.

At this point it seemed best to compare the growth of abutilon seedlings in these favorable dilutions of magnesium sulphate with the growth

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in similar dilutions of a calcium salt. Two parallel series were started, each consisting of seven cultures; the one magnesium sulphate and control, the other calcium nitrate and control. *Table* 4 gives a summary

TABLE 4

Series 4 with abutilon seedlings and magnesium sulphate, and abutilon seedlings with similar solutions of calcium nitrate. Experiment was started March 12, 1906. Average growth for 120 hours given in millimeters. H = hypocotyl. R = root. Average temperature 57°F.

Culture		Sec. Rts. appeared	Growth in 120 hours	Condition Mar. 17
Water	1.	5th day	23.9 { H.21.6 R. 2.3	Normal, sec. rts. short
	2.	5th day	20.6 { H.18.3 R. 2.3	Normal, sec. rts. short
m 8192	$MgSO_4$	5th day	30.9 { H.22.6 R. 8.3	Normal, sec. rts. short
	$Ca(NO_3)_2$	5th day	28.6 { H.22.6 R. 6.	Normal, sec. rts. short
m 16384	$MgSO_4$	4th day	38.5 { H.25.9 R.12.6	Normal, sec. rts. 0.8-1 mm.
	$Ca(NO_3)_2$	5th day	30.6 { H.24. R. 6.6	Normal, sec. rts. 0.5 mm.
m 32768	$MgSO_4$	4th day	59.9 { H.24.3 R.34.6	Normal, sec. rts. 1 mm.
	$Ca(NO_3)_2$	5th day	25.9 { H.21.3 R. 4.6	Sec. rts. just started on No. 2
m 65536	$MgSO_4$	4th day	53.9 { H.25.3 R.28.6	Normal, sec. rts. 0.8 mm.
	$Ca(NO_3)_2$	5th day	18.6 { H.14.6 R. 4.	Normal, sec. rts. just started
m 131072	$MgSO_4$	4th day	35.6 { H.21. R.14.6	Normal, sec. rts. 0.5 mm.
	$Ca(NO_3)_2$	5th day	29. { H.24.5 R. 4.5	Normal, sec. rts. just started
m 262144	$MgSO_4$	5th day	39.3 { H.21. R.18.3	Normal, sec. rts. 0.5 mm.
	$Ca(NO_3)_2$		24. { H.20. R. 4.	Normal, no sec. rts.

of the results. It is seen that throughout the series, the growth of seedlings is greater in the magnesium sulphate solution than in the corresponding dilution of calcium nitrate. This is not because of the toxicity of the calcium nitrate, the toxic point having already been established at concentrations above *m*/1024; and besides, the seedlings were as healthy as those in water. It is evident that calcium ceases to be stimulating in the dilutions at which magnesium no longer exhibits toxicity but reaches its greatest stimulative power. The stimulating effect of the magnesium sulphate was most noticeable in the root growth; in *m*/32768 being fifteen times that in the control, and eight times that in the calcium nitrate culture of the same dilution. The secondary roots appeared sooner in the magnesium sulphate cultures and reached a greater growth. Hence it again becomes evident that in certain concentrations, both calcium salts

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and magnesium salts are toxic. It is also certain that in the case of both magnesium and calcium, there is a dilution at which the toxic action ceases and stimulation begins. For abutilon seedlings in the case of magnesium this point seems to be at a concentration approximately equal to that of an *m*/8192 solution of magnesium sulphate.

In order to be sure beyond doubt that the stimulating effects noted in the preceding experiments were not due to any impurity in the salt used, a new Kahlbaum product was carefully analyzed and another stock solution made from this tested salt. Another series was grown in cultures prepared from this solution, and the results were in accordance with those obtained in previous trials. A summary of these results is given in *table* 5.

TABLE 5

Series 5 with abutilon seedlings and magnesium sulphate. Experiments were started October 27, 1906. Average growth given in millimeters.
H. = hypocotyl. R. = root. Pl. = plumule.

Culture	Sec. Rts. appeared	Growth in 168 hours		Condition on Nov. 7
Water	5th day	32.9	H.31.6 R. 1.3	Roots dead and flaccid
$MgSO_4$				
m/8192		32.3	H.29. R. 3.3	Pl. just started
m/16384	3rd day	45.3	H.37.66 R. 7.6	Pl. started in all, partly dried cotyls in 2 and 3, good sec. roots
m 32768	3rd day	49.3	H.40.3 R. 9.	All healthy, color good, pl. started strong sec. roots
m/65536	2nd & 3rd day	41.2	H.35.6 R. 5.6	Cotyls dried on No. 2, others healthy, color not so good as in last, pl. just started
m/131072	3rd day	56.6	H.38.3 R.18.3	All healthy, pl. started, good sec. roots
m/262144	2nd & 3rd day	43.3	H.36.3 R. 7.	All healthy, pl. started; good sec. roots
m/524288	3rd day	43.6	H.36. R. 7.6	No. 1 and 2 healthy except a black spot on one cotyl. Pl. smaller than in preceding

As in former experiments the growth was stimulated by the magnesium sulphate, with the exception of the *m*/8192 solution. The growth in this instance was 0.7 mm. less than in water, and secondary roots did not appear; and at the end of three weeks, the roots were flaccid. Since the growth in all three seedlings was vigorous and uniform, the results were evidently due to the action of the magnesium. In *series 2*, the *m*/8192 solution produced a stimulation of 24.3 mm.; while in *series 1*, *3*, and *4*, the stimulation varied from 0.9 mm. to 10.7 mm. This fluctuation in result is not unusual for a molecular solution which, in its strength, is on the border between such as are toxic and such as stimulate. And it is also probable that the point of toxicity varies to a certain extent with the temperature.[1] The maximum stimulation in this

[1] According to Brooks in "Temperature and Toxic Action" (*Botan. Gaz.*, 42: 359, (1906) as related to spore germination, toxicity increases with the rise of temperature. Since these experiments with magnesium sulphate were not carried on at constant temperatures, no such definite conclusions can be drawn. But it is a point well worth considering.

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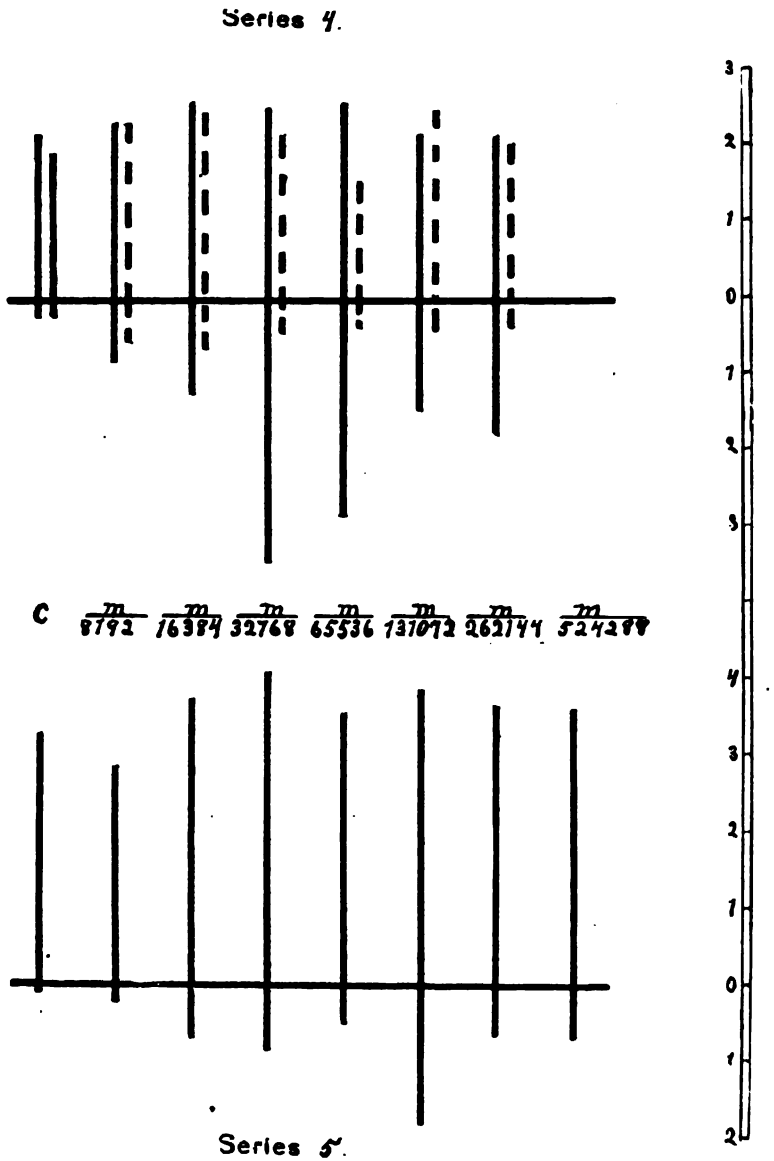


PLATE 2

Series 4: Diagram showing the comparison between the actual average growth during 120 hours, of abutilon seedlings in various concentrations of $MgSO_4$ and in similar concentrations of $(CaNO_3)_2$ with controls (*C*). The growth in $(CaNO_3)_2$ is indicated by broken lines.

Series 5: Diagram of growth illustrating table 5.
The root growth is shown below base line, the growth of hypocotyl above. The marginal units are in centimeters. The molecular fractions apply to both series.

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series occurred in *m*/131072. In dilutions beyond *m*/8192, secondary roots appeared from two to three days sooner than in the control. The plumule developed to a greater extent and the color was better. As in former cases, death in the magnesium sulphate cultures began in the cotyledons, while the roots remained vigorous for weeks. These results verified the previous conclusion that *in proper dilutions magnesium salts have a stimulating effect on the growth of abutilon seedlings.*

The *Abutilon* is a type of dicotyledonous plants having seeds with leafy cotyledons and little endosperm. As has been previously stated, the seedlings were transferred to the culture as soon as the seed-coat was shed, having at that time used the stored nourishment of the seed, so that a reserve food supply was eliminated as a factor. In order to determine whether the response to the presence of magnesium was due to peculiarities of this particular plant or to the type of seedling, experimentation was begun with seedlings of pea and corn. These seeds were washed and soaked in distilled water for twenty-four hours, then germinated in sphagnum. When the roots were from two to four centimeters in length, the seedlings were transferred to the cultures. Throughout a series, however, seedlings having uniform growth were selected as far as possible. These were suspended from the bent points of glass rods supported over the mouths of beakers by sheet cork. Beakers of uniform size were used, each containing 300 cc. of a given solution, this being renewed as in previous experiments at the end of 96 hours. The results of the first series with pea seedlings are shown in *table* 6.

TABLE 6

Series 6, with pea seedlings and magnesium sulphate. Experiment was started Oct. 26, 1906. Average root growth in millimeters.

Culture	Sec. Rts. appeared	Growth in 168 hours	Condition on Nov. 7
Water	3rd day	37.33	Growth nearly stopped, sec. rts. up to 19 mm. long
$MgSO_4$			
m/8192	3rd day	24.66	Root growth stunted, gr. ceased, sec. rts. few, up to 14 mm. long
m/16384	3rd day	66.33	Growth very active, sec. rts. up to 23 mm. long
m/32768	3rd day	71.33	Growth very active, sec. rts. up to 28 mm. long
m/65536	3rd day	59.33	Growth active, sec. rts. up to 20 mm. long
m/131072	3rd day	63.33	Growth active, sec. rts. up to 18 mm. long
m/262144	4th day	62.	Growth active
m/524288	3rd day	52.66	Growth active, sec. rts. up to 18 mm. long

This experiment was twice repeated, extending the dilution one point farther each time, in order to ascertain at what dilution the stimulating effect would fail to occur. The *m*/8192 solution was universally toxic to the pea seedlings, stunting the growth of the primary root, and preventing the normal development of lateral roots. In fact, there was very little lengthening of the primary root after 96 hours. In series 6 and 8 however, at the end of two weeks, the lateral roots had attained a growth

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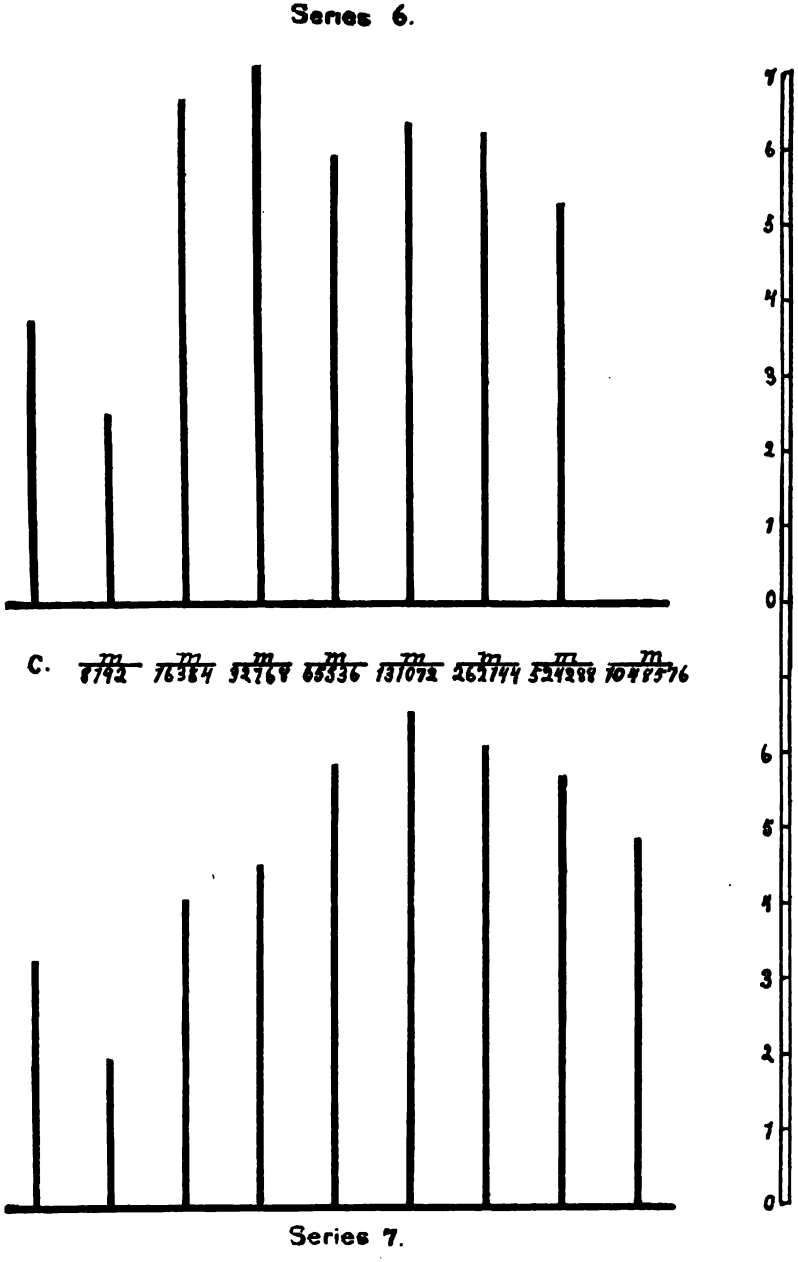


PLATE 3.

Diagrams showing the actual average root growth during 168 hours of the pea seedlings in the control (*C*) and the different concentrations of $MgSO_4$, Series 6 and 7. The marginal units are in centimeters. The molecular fractions apply to both series.

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greater than in any of the other seedlings. This may have been due to the added stimulation produced by the inhibition of the primary root, or it is possible that the cells of the root may have become acclimated to the magnesium sulphate so that the action was no longer toxic.

While *m*/8192 was toxic, decided stimulation was shown in *m*/16384, becoming greater in concentrations up to *m*/131072, then falling off until in *m*/2097152, growth was little more than that in the control. Even here however, there was perceptible stimulation. The lateral roots developed best in *m*/262144, forming in the course of five or six weeks, a branched system. In series 7 the root tips in the control were flaccid at the end of one week, and, in every instance, very little growth took place in the control seedlings after 168 hours; while growth in the magnesium sulphate cultures continued for four or five weeks longer. *Table* 7 gives a summary of the growth results in the three series.

TABLE 7

Comparing the results obtained in series 6, 7 and 8, with pea seedlings and magnesium sulphate. The growth for 168 hours is indicated in millimeters.

Culture	Average growth of seedlings in series 6	series 7	series 8	Total Average
Control	37.33	32.1	30.5	33.31
$MgSO_4$				
m/8192	24.66	19.66	15.25	19.8
m/16384	66.33	40.33	42.25	49.6
m/32768	71.33	45.5	45.75	54.19
m/65536	59.33	58.25	34.75	50.1
m/131072	63.33	65.75	45.75	58.2
m/262144	62.	61.25	37.	53.4
m/524288	52.66	57.25	39.	49.6
m/1048576		48.25	33.	41.29
m/2097152			40.25	40.25
Sec. rts. appeared	3rd day	2nd day	2nd day	
Max. Gr. Sec. Rts.	*m*/32768	*m*/262144	*m*/262144	
Avg. length of seedlings at start.	32.	25.8	36.2	

In the experiments with corn the same methods were followed as with the pea seedlings. In both series with corn, the greatest growth was in the *m*/32768 magnesium sulphate solution, in series 9 being double that in the control, while the *m*/8192 solution produced a vigorous growth, and the root tips were very active, as shown by the secretion at the tip. In dilutions greater than *m*/524288 there was no stimulation. In series 10, *m*/1024 was taken as the greatest concentration. Even in this, the toxic action, with one exception, was indicated only in the abnormal secretion at the root tips. This secretion was noticeable at the end of 24 hours, appearing as a large glutinous drop on the end of the root, when the seedling was lifted from the solution. The secretion diminished

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in solutions of less concentration, being absent in dilutions greater than *m*/8192. The results of both series are given in *table* 8. (page 1108).

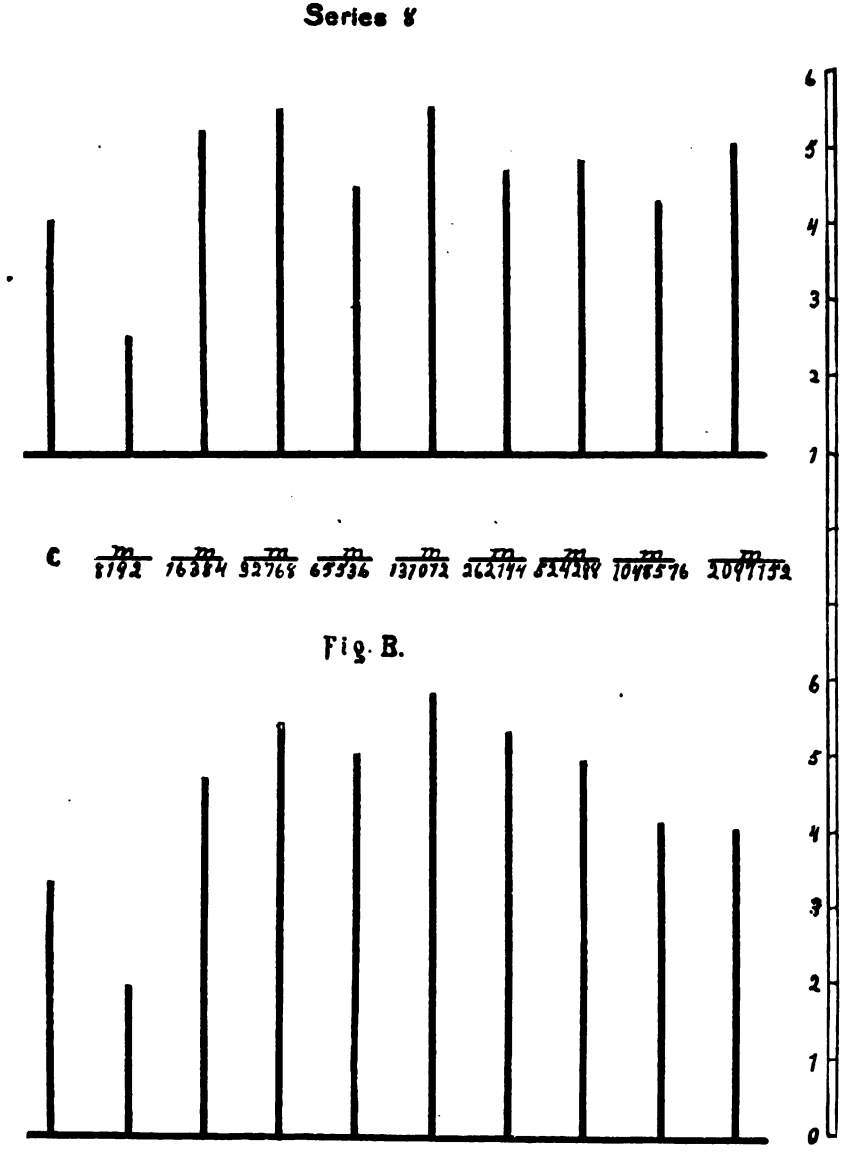


PLATE 4

Series 8: Diagram showing the actual average growth during 168 hours, of pea seedlings in the control (*C*) and in the different concentrations of $MgSO_4$. *Fig. b.*: Diagram showing the actual average root growth of the pea seedlings in series 6, 7, and 8. The marginal units are in centimeters. The molecular fractions apply to both series.

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TABLE 8

A comparison of the growth in series 9 and 10 with corn seedlings and magnesium sulphate. Series 9 started Nov. 12, series 10 started Nov. 28. Average growth of seedlings for 168 hours given in millimeters. 3 seedlings grown in each of series 9, 4 seedlings in series 10.

Culture	Growth for 168 hours Series 9	Series 10[1]	Remarks on growth
Water	70	83.75	
$MgSO_4$			
m/1024		87	Abnormal secretion at tip
m/2048		95	Abnormal secretion at tip
m/4096		75.5	Secretion less than above
m/8192	133	96.25	Roottip very active
m/16384	135.3	97.25	Root hairs on this and *m*/8192
m/32768	146.5	125.5	Maximum stimulation
m/65536	114.5	96.75	
m/131072	120.3	75.5	
m/262144	102	89.75	
m/524288	59.3	84	Two roots curled in series 9
m/1048576	57		One root curled
m/2087152	69		Normal, no stimulation
Avg. Temp.	65°F.	61.9°F.	
Range	48°–75°F.	49°–73°F.	Lateral roots appear 6th day

Comparison of the daily growth rate throughout series 1–10, shows the growth rapid for the first 48 hours, then diminishing in rate for the next 48, and after the renewal of the solutions, increasing in the magnesium sulphate cultures above *m*/8192, while the growth rate in the control seedlings either remained the same or diminished. (See *table* 9).

TABLE 9

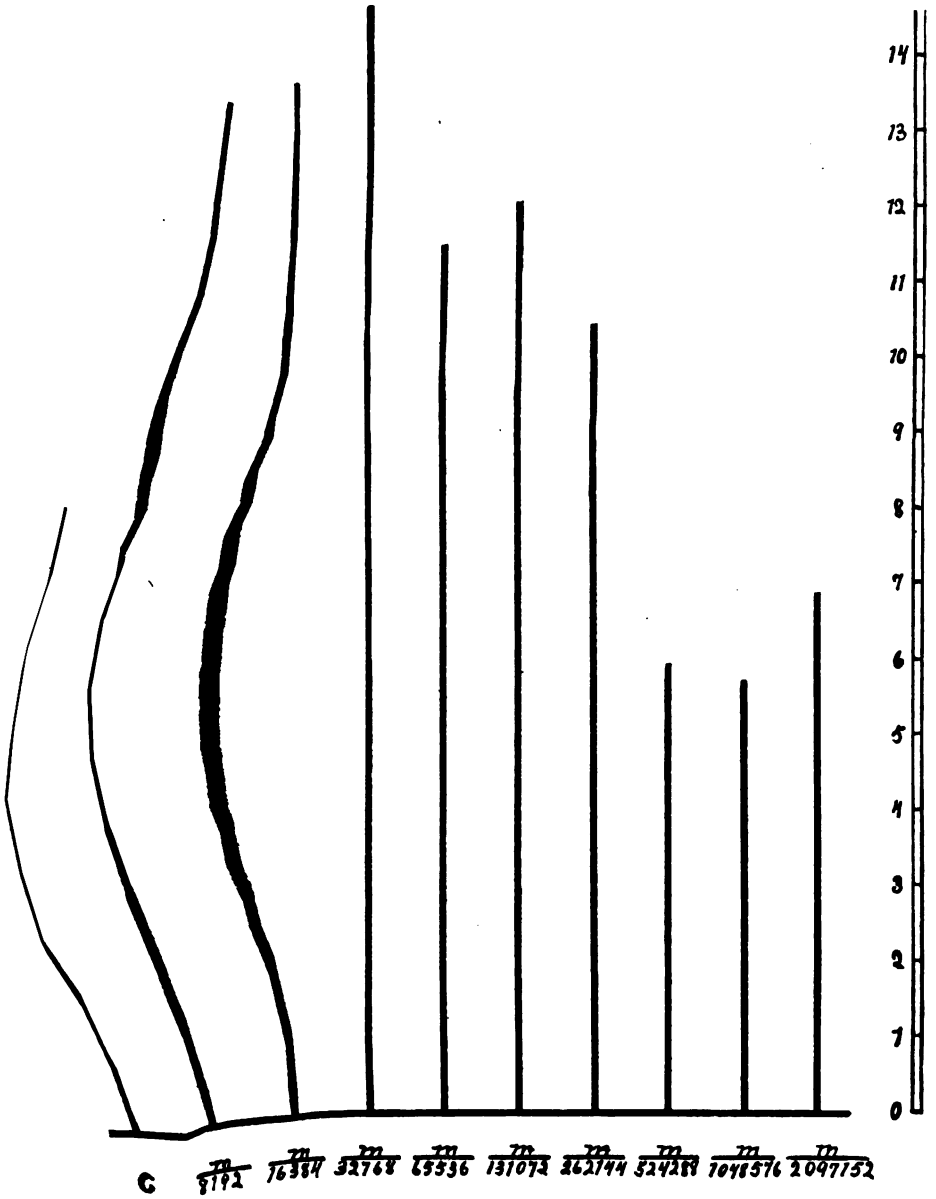
Showing the comparative daily growths in series 9 with corn seedlings and magnesium sulphate. The growths in each case represents the average of the three seedlings. Measurements in millimeters.

Culture	1st 24 hrs.	2nd 24 hrs.	3rd 24 hrs.	4th 24 hrs.	5th 24 hrs.	6th & 7th 24 hrs.
Water	11.5	13.8	16.5	6.66	6.16	13.66
$MgSO_4$						
m/8192	12.	15.33	21.66	15.	15.66	53.3
m/16384	11.3	16.66	18.	22.3	17.66	49.3
m/32768	11.	13.6	21.5	18.	19.5	58.
m/65536	10.	16.	19.66	13.3	11.3	43.3
m/131072	14.3	21.3	23.6	14.3	15.	31.75
m/262144	12.6	22.6	25.3	14.	6.6	20.

In the 10th series with corn seedlings, the solutions were not changed at the end of 96 hours, with the result that the growth rate in the magnesium cultures was below that in the control at the end of 168 hours. On the ninth day, however, the solutions were renewed for *m*/8192, *m*/32768 and the control. Measurements were taken for 72 hours; the

[1] The solutions were not changed at the end of 96 hours in series 10, and the growth during the last 72 hours was much less than in series 9.

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Series 9.

PLATE 5

Diagram showing the actual average root growth during 168 hours of corn seedlings in the control (*C*) and in various concentrations of $MgSO_4$, series 9. The marginal units are in centimeters.

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rate increased in *m*/32768, remained about the same in *m*/8192, and continued to fall in the control. It might be concluded that the gradual fall in rate after the first 48 hours was due to the increasing concentration of the solutions from loss of water. This idea is controverted by the fact that seedlings left for several weeks in solutions which are at first slightly toxic, will gradually gain upon the control. This was notably shown in *m*/1024, series 10, with corn seedlings. At the end of the first week the growth was about the same as the control. The seedlings were allowed to grow in the same solution for three weeks more, when the growth was nearly double that in the control. The same response has already been noted in pea seedlings grown in magnesium sulphate solution *m*/8192, in which case long secondary roots developed when the seedlings were left in the same solution for several weeks. These results would seem to indicate that the magnesium sulphate was gradually removed from the solution and utilized by the plants. (See *table* 10).

TABLE 10

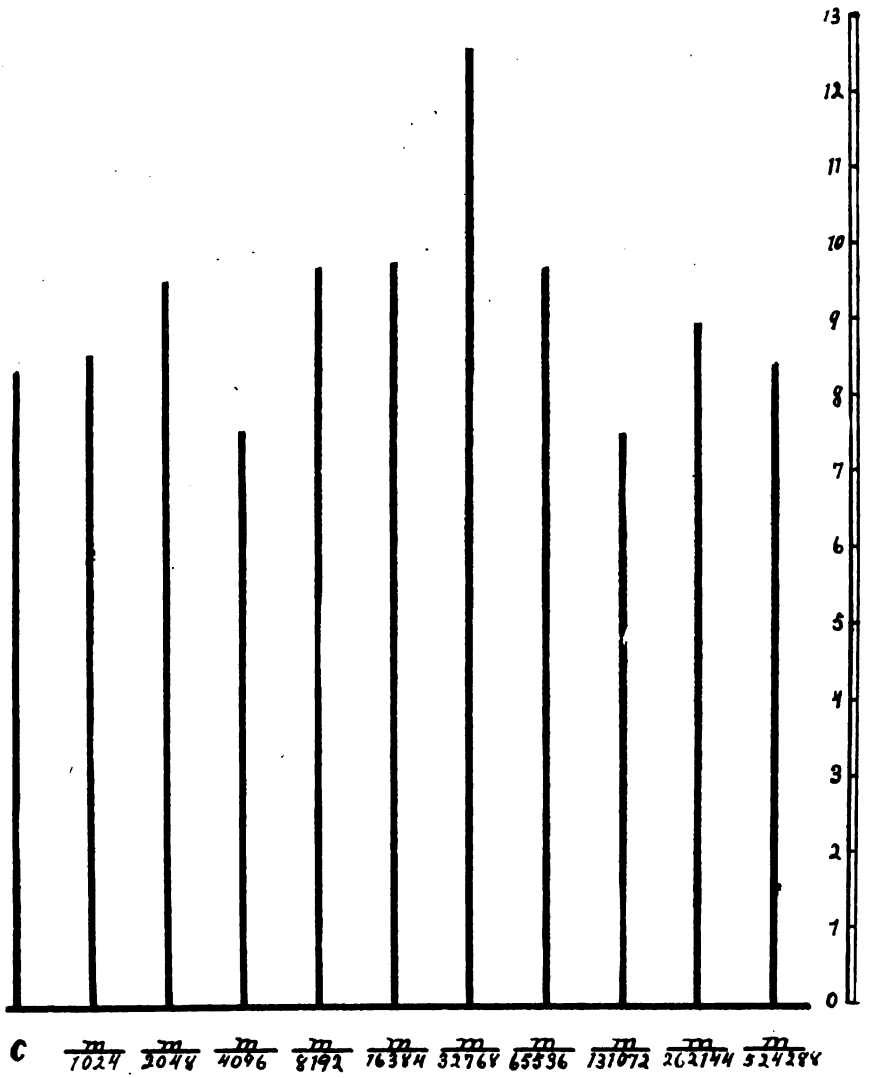
Comparison between daily growth rate in control, *m*/8192, and *m*/32768 series 9 and 10, corn seedlings and magnesium sulphate; the fluid having been changed at the end of 96 hours in series 9, but not until the 9th day in series 10. Average growth given in millimeters.

Culture	series.	1st & 2nd 24 hrs.	3rd 24 hrs.	4th & 5th 24 hrs.	6th & 7th 24 hrs.	8th & 9th 24 hrs.	10th 24 hrs.	11th & 12th 24 hrs.
Control	9.	25.3	16.5	12.8	13.6			
Control	10.	32.	15.	19.	20.75	12.	3.75	2.75
MgSO								
m/8192	9.	27.3	21.6	30.6	53.3			
m/8192	10.	40.7	20.5	20.7	15.	10.5	4.75	7.25
m/32768	9.	24.6	21.5	37.5	58.			
m/32768	10.	46.	26.	34.2	19.2	17.	8.75	21.75

Summary of Conclusions

Magnesium sulphate in solutions of greater concentrations than *m*/8192 has a toxic action on most seedlings, the degree of toxicity varying with the type of seedling and with the conditions. An *m*/8192 solution is toxic to pea seedlings, slightly stimulating to *Abutilon*, while it has a marked stimulating effect on corn seedlings. Maximum stimulation in magnesium sulphate results in solutions from *m*/32768 to *m*/131072, the point again varying according to the kind of seedlings grown. When magnesium sulphate is used in proper dilutions there may be produced a total growth nearly double that in the control; or in the case of *Abutilon* seedlings, a growth of the primary root 15 times that in the control. Not only is the growth of the primary root increased, but the lateral roots develop sooner, are more numerous, and attain a greater growth. Furthermore the stimulation is not limited to the root system, but the magnesium forces a more rapid and a greater growth of the hypocotyl

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Series 10.

PLATE 6

Diagram showing the actual average root growth during 168 hours, of corn seedlings in the control (*C*) and in the various concentrations of $MgSO_4$, series 10.
The marginal units are in centimeters.

and plumule. In these same concentrations, calcium nitrate causes very little stimulation.

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In addition to the marked stimulation which magnesium sulphate causes when it is used in dilutions from *m*/16384 to *m*/524288, it increases the vitality of the seedlings. The seedlings grown in the magnesium sulphate outlived those in the control by two or three weeks, and in some cases by a greater period.

From the foregoing results and conclusions, it is then evident that magnesium sulphate, in the absence of other salts, is not necessarily injurious in its effects, but on the other hand may be highly beneficial; while any *inhibitory* action is due to the presence of a relatively *large proportion* of magnesium in the solution.

Lastly the writer wishes to acknowledge the assistance of Dr. William J. Gies under whose direction these experiments have been carried on in the laboratories of the New York Botanical Garden.

[CONTRIBUTION FROM THE DIVISION OF FOODS, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE].

STUDIES ON APPLE JUICE.

BY H. C. GORE

Received May 17, 1907.

Experimental work on the preparation of unfermented apple juice was carried out during the past season at the large fruit farm of Mr. Isaac Pollard at Nehawka, Nebraska. The results of this work are given in the Year-Book of the Department of Agriculture for 1906. Very briefly the method which was developed for the preparation of the juice consisted first in removing the sediment from the juice of the fresh fruit by passing it twice through a milk separator. The juice was then carbonated if desired, canned, or bottled, and finally sterilized by heating for short periods of time at temperatures not exceeding 70°.

Other lines of work relating to apples were carried on at the same time and as the literature on the chemistry of this important fruit in America is rather meagre, it is believed that the data here presented will be of interest.

Analyses of the following juices were made:

(a) Juices of the cull apples employed for cider making.

(b) Juices from the cider-mill at various times during the season.

(c) Juices of standard varieties of apples grown at Nehawka.

(d) Juices of summer apples in regard to their value for vinegar stock.

(e) Juices of decaying apples.

The methods employed were briefly as follows: Solids were determined by the Brix spindle. This method has been shown by Browne[1] to be quite accurate for fruit juices. Determination of acid: ten gram samples of juice were diluted with distilled water, heated to boiling, and titrated with tenth normal alkali, using phenol phthalein as indicator. Sugars were

[1] This Journal, 23, 875.

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TABLE I

ANALYSES OF JUICES OF CULL APPLES

Variety and condition of sample	Date of Picking 1906	Date of Analysis 1906	Weight per apple grams	Solids per cent	Acid as Malic per cent	Reducing Sugar as invert percent	Total Sugar as invert percent	Sucrose per cent	Undetermined solids
Maidens' Blush, over-ripe		Aug. 22	135.9	11.77	.14	5.74	9.62	3.69	2.20
Porter "		" "	113.3	13.30	.25	7.06	10.15	2.93	3.06
Wealthy, over-ripe and undersized		" "	95.2	11.75	.27	6.50	9.02	2.39	2.59
Florence crab, over-ripe, very mealy	Aug 21	" "	30.6	16.97	.87	11.40	11.66	.25	4.45
Dyer, over-ripe		" "	145.0	14.17	.43	7.50	10.63	2.97	3.27
Porter, unripe and undersized		" "	45.0	9.52	.28	6.04	6.94	.85	2.35
Autumn Strawberry		" 24	105.5	11.64	.22	6.91	9.45	2.41	2.10
Haas		" "	102.0	12.79	.59	6.36	9.70	3.17	2.67
Fall Winesap, undersized	Aug 27	Sept. 2	77.2	13.18	.64	6.81	10.21	3.23	2.50
Wolf River, wormy	" 24	" "	275.0	12.93	.69	6.74	9.59	2.71	2.79
Pound Sweet, wormy or damaged by hail	" 28	" "	220.0	12.63	.04	7.84	10.25	2.29	2.46
Seek-no-further, undersized	" 28	" "	76.0	12.64	.52	7.27	9.43	2.05	2.80
Yellow Bellflower, undersized or wormy	" 29	" "	146.2	14.09	.60	7.84	10.66	2.68	2.97
Northern Spy, wormy		" "	213.7	13.24	.69	7.07	10.10	2.88	2.60
Fameuse, undersized		" 10		13.67	.59	8.33	10.32	1.89	2.86
Shackleford, undersized		" "		11.87	.42	6.31	8.53	2.01	3.13
White Bellflower, wormy or damaged by hail		" "		12.42	.54	5.90	9.25	3.18	2.80
" " undersized	Sept. 11	" 17	121.2	13.06	.46	7.97	10.51	2.41	2.22
Tolman, undersized	" "	" "	58.5	13.07	.12	7.92	10.40	2.36	2.67
Grimes, undersized	" 12	" "	60.6	13.76	.47	7.04	10.49	3.28	2.97
Northwestern Greening, wormy or damaged by hail	" 22	" 28	184.5	12.68	.44	7.45	9.99	2.41	2.38
Rhode Island Greening, wormy	" 25	" "	211.3	12.03	.50	6.30	10.54	4.03	1.20
Scott Winter, wormy or damaged by hail	" "	" "	114.3	12.68	1.32	6.26	9.38	2.96	2.14
York Imperial, wormy or undersized	Oct. 2	Oct. 13	79.0	13.15	.55	7.18	9.85	2.54	2.88[1]
Jonathan, undersized	" "	" "	63.6	14.32	.55	8.50	13.72	4.96	.31
Missouri, undersized	" "	" "	48.8	16.17	.74	8.36	12.43	3.87	3.20
Ben Davis, Wormy	" 5	" "	101.9	12.45	.63	6.50	9.50	2.85	2.47
Roman Stem, Wormy	" 6	" "	99.7	14.17	.57	6.46	11.35	4.65	2.49
Winesap, Wormy	" 13	" "	97.9	12.85	.62	7.29	10.09	2.66	2.28
Maximum				16.97	1.32	11.40	13.72	4.96	4.45
Minimum				9.52	.04	5.74	6.94	.25	.31[1]
Average				13.07	.50	7.20	10.13	2.78	2.58

[1] See P 1114.

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determined by the gravimetric method, using the tables of Munson and Walker[1], and alcohol by the official method of the Association of Official Agricultural Chemists[2]. The value called undetermined solids is the difference between the solids, and the sum of the acid, reducing sugar, and sucrose.

(a) Culls are apples which cannot be marketed, and are, therefore, used by the cider mills. At the packing house, apples were rejected for market purposes for a variety of reasons. They were either over-ripe for packing, wormy, or otherwise injured, or under-sized—less than two inches in diameter. Samples of these apples were taken from the packing house as often as new varieties were received. Care was taken in all cases to secure representative samples consisting of about a peck of apples. For analysis the samples were ground in a meat chopper and received in a cloth bag, from which the juice was expressed by pressure. The analyses of the juices are given in Table 1. Generally speaking, the juices of these apples became richer in sugar and acid as the season progressed. The undetermined solids, consisting of nitrogeneous matter, tannin, ether extract, pectin, and ash, remained practically constant during the season. The low value shown for the Jonathan variety is probably due to an error in determining the solids. Attention is called to the high acid content of the variety Scott's Winter. The variety is unique in this respect. The flavor of the fruit was remarkably sharp, and very agreeable.

(b) The juices from the mill were analyzed at intervals during the season. Like the juices of the cull apples, the mill juices increased gradually in sugar content and acid. The analyses are given in Table 2. Ow-

TABLE 2

COMPOSITION OF MILL JUICES

Description	Date 1906	Solids per ct.	Acid as Malic per ct.	Reducing Sugars as Invert per ct.	Total Sugars as Invert per ct.	Sucrose per ct.	Undetermined Solids per ct.
Early Fall Apples	Aug. 13		.24	7.02	8.45	1.34	
	" 27	11.85	.36	7.67	9.46	1.70	2.12
	Sept. 5	11.14	.30	6.38	8.36	1.88	2.58
	" 12	11.33	.38	7.50	9.25	1.66	1.79
Largely Grimes Golden	" 13	12.30	.24	7.62	10.15	2.40	2.04
	" 27	12.88	.39	7.72	10.45	2.59	2.18
Largely Ben Davis	Oct. 2	13.00	.50	7.82	10.28	2.34	2.34
	" 6	12.45	.57	7.01	9.92	2.76	2.11
	" 8	13.40	.54	7.36	10.74	3.21	2.29
	" 11	13.09	.52	6.24	10.10	3.67	2.66
Maximum		13.40	.57	7.82	10.74	3.67	2.66
Minimum		11.14	.24	6.24	8.36	1.34	1.79
Average		12.38[1]	.40	7.23	9.72	2.35	2.23[1]

[1] Average of 9 determinations.

[1] This Journal, 28, 663.

[2] U. S. Dept. of Agr., Bur. of Chem. Bull., 46, p. 57.

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ing to the fact that the mill ran irregularly and that wind-falls and custom apples were constantly being mixed in the bins with the culls from the packing house, no comparison between the composition of the mill juice and that of the juice from cull apples is possible.

(c) Samples of eleven standard varieties grown at Nehawka were secured when the main crop was picked and the juice of the fruit was analyzed when the apples became ripe, that is, when the starch of the apples had practically disappeared. Some samples, indeed, were quite overripe at the time of analysis, showing mealiness or withering, and probably some loss of acidity. The results of these analyses are given in Table 3.

TABLE 3.

ANALYSES OF JUICES OF RIPE FALL AND WINTER APPLES GROWN AT NEHAWKA, NEB.

	Wt. per Apple Grams.	Solids per cent.	Acid as Malic per cent.	Reducing Sugar as Invert per cent.	Total Sugar as Invert per cent.	Sucrose per cent.	Undetermined Solids per cent.
Gano[1]	169.8		.38	6.79	10.27	3.31	...
York Imperial	153.6	12.57	.43	7.82	10.84	2.87	1.45
Arkansas	162.7	13.44	.45	8.89	11.82	2.78	1.32
Roman Stem[1]	127.5	14.79	.36	7.64	12.97	5.06	1.73
Wine Sap	112.9	14.14	.43	8.95	11.49	2.41	2.35
Rhode Island Greening[2]	156.0	11.99	.57	7.45	10.26	2.67	1.30
White Winter Pearmain	209.2	12.59	.46	5.55	10.95	5.13	1.45
Grimes Golden[3]	101.3	13.19	.28	7.42	12.08	4,43	1.06
Fameuse[2]	92.2	13.89	.34	8.87	11.50	2.50	2.18
Jonathan[2]	99.8	13.74	.40	9.65	11.93	2.17	1.52
Ben Davis[1]	157.8	12.02	.48	7.50	11.25	3.56	.48
Average		13.24[4]	.42	7.87	11.40	3.35	1.48

The average of the analyses in Table 3 is compared in Table 4 with the averages of analyses of juices of Eastern grown apples, compiled by Van Slyke[5]. From the table it will be noted that the solids and sugar content of Nebraska apples are practically the same as the solids and sugar content of apples grown in Eastern states. An exception is to be noted, however, in the case of the New York apple juices, since these seem to be considerably richer than other apple juices in solids and sugar. The Nebraska apple juices were slightly poorer in acid than juices from the Eastern apples, but this is probably accounted for by the fact that the

[1] Mealy.
[2] Slightly mealy and slightly withered.
[3] Slightly withered.
[4] Average of 10 determinations.
[5] N. Y. Exp. Sta. Bull., 258, p. 419.

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samples analyzed were somewhat over-ripe, since loss in acidity is known to occur under these conditions.

TABLE 4

AVERAGE ANALYSES OF APPLE JUICES FROM DIFFERENT LOCALITIES

Locality	Specific Gravity	Solids	Acid as Malic	Reducing Sugars	Total Sugar as Invert	Sucrose	Ash	Number of Analyses
Nebraska.....		13.24	.42	7.87	11.40	3.35	..	11
New York[1]	1.064	15.11	.53	9.28	13.33	3.85	.23	13
Pennsylvania[1]	1.056	13.31	.58	7.67	11.47	3.61	.28	11
Virginia[1]	1.053	13.31	.52	7.00	10.41	3.35	..	77
Washington, D.C.[1].....	1.054	13.39	.51	6.84	10.00	3.48	.33	21

(d) Summer apple juices are not considered by growers to be of value for vinegar stock, owing to the difficulty of preparing a vinegar of standard strength. The juices are rather low in sugar and the alcoholic fermentation usually takes place at summer temperatures. If the surface of the juice is freely exposed to the air acetic fermentation is almost sure to develop, since, as is well known, summer temperatures favor the growth of acetic acid bacteria. Acetic acid, so formed will retard the alcoholic fermentation, or even stop it entirely. This is well known from the work of La Far.[2] The resultant product will contain unfermented sugar, and as the juice originally contained only barely enough sugar for standard vinegar, the vinegar produced will be low in acetic acid.

At Nehawka, an opportunity was offered to study two varieties of summer apples with regard to their value as vinegar stock. Two lots of juice from culls consisting of over-ripe Early Harvest and Duchess apples were prepared at the mill, and at once poured into clean 50 gallon barrels. Four barrels of Duchess and two barrels of Early Harvest apple juice were obtained. The barrels were closed with cotton plugs, and the fermentation was carried on in a room at a temperature of about 70° F., with and without the addition of pressed yeast in the different experiments. Space was left in each barrel for the formation of a head. In all cases fermentation set in rapidly. Heads formed which foamed over, resulting in some loss of liquid. As soon as the heads subsided fresh cotton plugs were inserted so as to retain the protective layers of carbon dioxide gas on the surfaces of the ciders. At the end of twenty days[3], alcohol, acid, and solids were determined. The analyses of the original juices and those made on the cider are given in Table 5. The results show that nearly the theoretical yield of alcohol can be readily obtained from these juices by fermentation. The usual loss of acid incident to fermentation of fruit juices by yeast is shown. The addition of pressed yeast increased the

[1] Taken from the summary of analyses compiled by Van Slyke, loc. cit.

[2] Landw. Jb. 1895, 24, 445.

[3] The fermentation was doubtless completed before this time, but owing to other work the juices were not analysed as soon as dry.

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yield of alcohol only slightly. The dry cider obtained could probably have been handled successfully in a quick process generator to produce vinegar of 4 per cent. strength. The vinegar so produced, however, would have been quite low in solids.

TABLE 5.

ANALYSES OF FRESH AND FERMENTED JUICE OF SUMMER APPLES.

Description of Sample.	Rate of Analysis, 1906.	Solids, per cent	Acid as malic per cent.	Reducing Sugar as Invert per cent.	Sucrose per cent.	Alcohol gr. 100 lbs.	Pressed Yeast added per bbl.
Duchess Apple Juice, pressed July 31	Aug. 23[1]	10.54	.75	7.56	.35	—	—
Early Harvest apple juice, pressed July 31	"	10.84	.42	8.06	.57	—	—
Duchess apple cider, fermented by wild yeast	" 20	1.99	.28	.11	—	3.82	—
Duchess apple cider, fermented by brewers' yeast.	"	1.61	.27	.09	—	4.05	⅛
Duchess apple cider, fermented by brewers' yeast.	"	1.77	.38	.06	—	4.21	¼
Duchess apple cider, fermented by brewers' yeast.	"	1.87	.44	.04	—	3.81	⅜
E. Harvest apple cider, fermented by wild yeast	"	1.85	.31	.11	—	4.09	—
E. Harvest apple cider, fermented by brewers' yeast.	"	1.55	.34	.12	—	4.34	¼

(e) This work has its practical significance in that at times when running a cider mill decayed apples are encountered and it is a question of some importance as to their value as vinegar stock and as to the influences of decayed apple juice on the juice of sound apples in regard to proper fermentation into vinegar. The question of the wholesomeness of vinegar made from decayed apple juices is not considered here.

Sample No. 25 was the juice of thoroughly decayed summer apples which were taken from bins at the cider mill. The juice obtained had an odor of acetic acid, but possessed no disagreeable, musty odor or taste. Its analysis is given in Table 6. This sample served to indicate the general character of the changes which ensue on decay. The sucrose originally present was practically all inverted. The total sugar, of which about 8 per cent. was probably present before decay set in, was considerably lessened in amount and 0.75 per cent. alcohol and 0.67 per cent. of acetic acid were found. The character of the changes, therefore, would seem to be similar to those which go on when a fruit juice is fer-

[1] These juices were not analyzed at once, owing to lack of laboratory facilities. Samples were therefore preserved by addition of sodium benzoate, and analyzed later. On this account the values for sucrose are probably a little lower, and those for reducing sugars a little higher than the true values, due to inversion of sucrose on standing.

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mented into vinegar except that the inversion of the sucrose, the formation of alcohol, and its oxidation into acetic acid go on more or less simultaneously.

TABLE 6

CHEMICAL CHANGES IN JUICE OF DECAYING APPLES

Serial No.	Description of Sample	Date of Analyses 1906	Acid as Acetic per ct.	Reducing Sugar as Invert per ct.	Total Sugar as Invert per ct.	Sucrose per ct.	Alcohol gr. per 100 cc.
25	Juice from decayed apples.....	Aug. 28	.67	5.67	5.76	.09	.75
43	" " sound portions of apples	Sept. 8	..	7.32	10.13	2.67	none
44	" " decayed " " "	" 8	..	7.45	8.26	.77	none
67	" " sound apples	" 18	.22	7.00	8.79	1.70	none
68	" " decayed apples	" 18	.12	7.56	7.83	.26	.28
96	" " " "	Oct. 9	2.18	2.80	2.86	.06	.47

Samples 43 and 44 were juices from sound and decayed portions respectively of ripe Autumn Strawberry apples. Partly decayed fruit was used and sound and decayed sections from opposite sides of each apple were used for the two samples.

These contrasting analyses served to show the character of the first changes which go on in decaying apples. The conspicuous changes were the inversion of sucrose and considerable loss of sugar. No alcohol had as yet been formed. Unfortunately acid was not determined.

Samples Nos. 67 and 68 were juices from sound and decayed apples, respectively, selected from a lot of over-ripe Autumn Strawberry Apples. The analyses show inversion of sucrose in the juice of the decaying apples, loss in sugar, and in addition, some formation of alcohol. They also show a notable lessening of acid. No acidification had as yet set in.

Sample 96 was a sub-sample from No. 68 which was allowed to decay further. It showed again, as did sample No. 25, the composition of decayed apples but in a more advanced stage. The sucrose was nearly all gone; there was present slightly less than 3 per cent. of reducing sugar, about ½ per cent. of alcohol, and over 2 per cent. of acetic acid. The presence of acetic acid is known to hinder alcoholic fermentation, and this accounts for the presence of unfermented sugar, La Far having shown that as little as ½ per cent. acetic acid may considerably retard fermentation by yeasts, while 1 per cent. entirely stopped alcoholic fermentation in case of 12 out of 15 races of yeasts which he studied.

The above analyses indicate the general course of the chemical changes which go on in decaying apples. Similar analyses, carried on with mycological control would probably give results of much interest. The tendency of decaying apples to yield juices rich in acetic acid is clearly shown. This fact must be considered as affecting unfavorably the value of the juice for vinegar stocks in view of the tendency of acetic acid to inter-

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fere with alcoholic fermentation. In other words the manufacture of a vinegar of standard strength may be seriously affected by an admixture of acetified apple juice with juice of sound apples.

THE ESTIMATION OF CELLULOSE IN WOOD BY THE CHLORINATION METHOD.

By A. L. Dean and G. E. Tower.

The chemical constitution of woody tissues presents a problem of great complexity. Any single sample of wood contains a number of complex compounds whose nature is but little understood. If all kinds of wood were chemically alike, or even if the wood from all parts of the same tree was identical, the study of woody tissue would be simplified. The older idea, especially the idea prevalent amongst botanists, was that the cell walls of woody tissues were composed of "cellulose" which became impregnated with "lignin." Later and more careful studies appear to have established the fact that the foundation of woody cell walls is not a simple cellulose, but a compound cellulose, to which the name lignocellulose, has been given. This lignocellulose may be split up into cellulose on the one hand, and the lignone group on the other. The cellulose which results from the cleavage differs to a marked extent from the normal type cellulose of the cotton fiber. The lignone complex appears to contain cyclical groups and to be related to the carbohydrates in no very definite fashion.

Besides the lignocellulose which makes up the major portion of wood, there are always present a number of different bodies which are apparently not chemically united to the lignocellulose. Amongst these substances two are prominent; the so-called wood gum, which may be extracted with cold dilute alkaline solutions, and the group of the ether soluble resins.

It was stated above that the lignocellulose might be split into the two constituent radicals, cellulose and lignone. This cleavage is not easily carried out quantitatively, inasmuch as the treatments which remove the lignone tend to attack the cellulose. The isolation of cellulose from wood is carried out on an enormous scale in the manufacture of paper pulp by the sulphite and soda processes. These methods are said to always involve some loss of cellulose, and unless carefully regulated the loss is likely to be great.

A number of methods have been elaborated for the estimation of the quantities of cellulose in vegetable cell walls. They are all tedious, and the cellulose obtained by several of them is apparently a variable and ill defined product. Cross and Bevan[1] have elaborated a method for the estimation of cellulose in the lignocellulose of jute fiber, a method which

[1] Cellulose: an Outline of the Chemistry of the Structural Elements of Plants. Cross and Bevan, London, 1895.

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appears to yield concordant and valuable results. In their method the lignocellulose is treated with chlorine gas, giving rise to a lignone chloride which is soluble in hot alkaline sulphite solutions. They do not give the results of the systematic application of this method to cellulose estimations in wood, although they imply that it is applicable to such tissues.

Sherman[1], in his study of the insoluble carbohydrates of the wheat, estimated the amount of cellulose in the lignocellulose of the wheat kernel. After trying out the methods of Schulze (potassium chlorate and nitric acid,) Lange (fusion with caustic alkalies), and the chlorination method of Cross and Bevan, Sherman concludes that this last method gives the most exact estimate of the cellulose and yields cellulose of maximum purity.

Cross and Bevan give the following directions.[2] "About 5 grms. of the fibre weighed after drying at 100°—are (*a*) boiled for 30 minutes with a dilute solution of sodium hydrate (1 per cent. NaOH), which is kept at constant volume by addition of water. The fiber is well washed on a cloth or wire gauze filter, squeezed to remove excess of water, opened out, placed in a beaker, into which (*b*) a slow stream of washed chlorine gas is passed. Rapid reaction ensues, and the fiber changes in color, from brown to a bright golden yellow. To ensure complete conversion of the lignone, it is necessary to leave the fiber for some time (from 30-60 minutes) in the atmosphere of Cl gas. (*c*) The chlorinated fiber is removed, washed once or twice with water to remove hydrochloric acid, and placed in a 2 per cent. solution of sodium sulphite; the solution is gradually raised to the boiling point, a small quantity of caustic soda solution is added (0.2 per cent. NaOH calculated on the solution), and the boiling continued for 5 minutes. (*d*) The cellulose is now thrown upon a cloth filter and washed with hot water. It will be found to be almost pure *i.e.* white; but to remove the last residues of the non-cellulose, it may be bleached by immersion in a dilute solution by hypochlorite (0.1 per cent. NaOCl for a few minutes, or treated with dilute permanganate solution (0.1 per cent. $KMnO_4$). It is well washed from these oxidizing solutions, treated with sulphurous acid on the filter, well washed with water, squeezed, dried and weighed."

In another place these authors state that in applying this process to wood, it is necessary to reduce the wood "to the finest possible shavings." In giving directions for obtaining cellulose from pine wood[3] they say that after treating the finely divided wood as in the above quoted passage, the chlorination must be repeated until pure cellulose is obtained.

It is, of course, impossible to follow the directions given above when

[1] Sherman: J. Am. Chem. Soc., 19, 291, 1897.
[2] Cellulose: p. 95.
[3] loc. cit: p. 244.

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using finely ground wood, since the quantitative removal of such a material from a gauze or cloth filter, without the use of a stream of water, is practically impossible. After some experimenting we adopted the following method of procedure.

The wood was dried out at a low temperature, 60°-80°, and ground in a hand mill. The material was then sifted through a sieve having twenty-four meshes to the inch. The wood powder obtained in this way was dried at 100°-105° and weighed portions of about five grams each used for each determination. The sample, after being boiled in 200 cc. of 1 per cent. sodium hydroxide solution for a half hour, was filtered with suction on a small perforated porcelain plate in a five-inch funnel. In order to hold the plate firmly in the funnel during the filtration and the subsequent manipulation, we passed a piece of fairly stiff silver wire up through one of the holes in the center of the plate and securely fastened it by bending the end down. The silver wire extended down through the stem of the funnel, projecting a quarter of an inch beyond the end. By putting one or two slight bends in the wire it can be made to bear against the walls of the inside of the stem, and the filter plate is held firmly in place. When the ground wood is first poured on to such a plate it behaves much like asbestos, some running through and the rest matting down and forming a coherent layer. The portions running through are then poured back, and by careful manipulation no significant loss of fiber occurs. The wood which had been boiled in alkali was washed on the filter with a large volume of water. The matted fiber was loosened up with a sharp pointed glass rod and the rubber tube leading from a chlorine generator attached to the stem of the funnel. A slow stream of washed chlorine gas was passed up through the material, which was occasionally stirred to allow a thorough penetration of the gas.

After the chlorination the funnel was returned to the suction flask and the fiber washed to remove hydrochloric acid. For the boiling in sodium sulphite solution it was necessary to remove the material to a casserole. This may be readily accomplished by inverting the funnel over the casserole and pushing on the silver wire projecting from the stem. The main mass of the material drops out and the remainder is readily washed from the funnel and filter plate with the aid of 150 cc. of 2 per cent. sodium sulphite solution which has been previously measured into a wash bottle. After bringing the sulphite solution to a boil, 3 cc. of a 10 per cent. sodium hydroxide solution were added and the mixture boiled for five minutes. The fiber was again collected on the filter plate, washed with hot water until the washings were colorless, and the product again chlorinated, or, when desired, bleached in the funnel by the use of 0.1 per cent. potassium permanganate solution followed by sulphurous acid.

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In order to conveniently weigh the final product it was transferred from the funnel to a beaker, with the aid of alcohol from a wash bottle, and then collected in a large, tared Gooch crucible, dried and weighed.

A single chlorination, even if prolonged for two hours, was insufficient to yield a white cellulose after permanganate bleaching. The greatest difficulty in the whole process lay in judging the end point. Finely ground wood is not homogenous, since there are always small pieces made up of cells from the summer wood of the annual rings, and these cells with their thick walls offer a marked resistance to reagents. It frequently happened that after a series of chlorinations and permanganate bleachings which reduced the great mass of the sample to white cellulose that there still remained particles which were yellow. Since treatment with chlorine gas will attack wood cellulose to some extent, it became questionable whether or not continued chlorination did not cause a loss of cellulose in the finer particles which introduced a greater error than that caused by stopping the treatment before the sample was uniformly white.

The lignocelluloses when immersed in a mixture of equivalent solutions of potassium ferricyanide and ferric chloride are stained blue with the fixation of both iron and cyanide groups. The gain in weight occurring in this reaction varies with the quantity of ferric ferricyanide solution which is used. Sherman found that with the same volumes and strengths of solutions, and the same time of immersion, the gain in weight was constant for a given sample. By applying the reaction to the cellulose obtained by the different methods, he obtained a criterion of their purity. Of the use of the reaction he says,[1] "the reaction with the ferricyanide solution seems of considerable value in testing the purity of celluloses. When the sample increases only slightly (about one per cent or less) in weight and is dyed only a bluish-green instead of a deep blue color, it is at least a very strong indication that lignin substances are not present in notable quantity."

In applying this reaction to the products obtained by us, we have followed Sherman's procedure: 10 cc. of 1.6 per cent. solution of ferric chloride were mixed with 10 cc. of a freshly prepared 3.3 per cent. solution of potassium ferricyanide; to this mixture 1 gm. of dry material was added and after standing one hour, with occasional stirring, the dyed fiber was collected on a Gooch filter, washed with water, dried, and weighed. In some cases the filtrate from the fiber was a deep green instead of the brownish-red color of the ferric ferricyanide solution, and it happened in a number of cases that a loss of weight followed the treatment, showing that soluble products were formed by the action of the ferricyanide solution on some of the constituents of the cellulose.

The results of the first series of estimations are given in Table I. After

[1] loc. cit.: p. 304.

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weighing out the samples of the more resinous woods, they were extracted with ether before the alkaline boiling.

TABLE I.

Wood	Length of Chlorination	Appearance of Cellulose	Per cent. of Cellulose	Per cent. gain with ferricyanide reaction
Longleaf Pine—sapwood	2 chlor. of 1 hr. & ½ hr.	Cream color	53.5	
" " "	4 " " ½ hr. each	white	53.8	
" " "	2 " " " " "	Light cream (uneven)	58.4	
" " heartwood*	3 " ¾ hr., ¾ hr. & ½ hr.	white	45.8	
" " "	3 " " " " " "	Light cream	49.0	
" " "	3 " " " " " "	Dark	52.8	
Loblolly pine—sapwood	3 " ½ hr. each	"	60.8	
" " "	2 " " " "	"	63.3	
" " "	3 " ½ hr. & 1 of ¾ hr.	white	53.9	
" " "	2 " " " " "	"	54.5	
" " heartwood*	2 " ¾ " 1 " ½ "	Light cream	49.6	3.80
" " "	3 " " "	" "	48.1	2.69
Lodgepole pine–sapwood	2 " " "	" "	59.4	6.71
" " "	2 " " "	" "	58.8	4.18
" " heartwood	3 " " " & 1 of ½ hr.	white	43.7	2.36
" " "	3 " " " " " "	Very white	40.4	4.05
" " "	2 " " "	Cream color	49.5	−.59
" " "	2 " " "	" "	50.4	−3.77
Spruce-mixed heart & sap	2 " ½ hr. & 1 of ¾ hr.	Light cream	59.6	3.94
" " "	2 " " "	Dark	63.8	6.07

*In boiling with Na_2SO_3 after the first chlorination of this sample the solution was made alkaline to 0.4 % instead of the usual 0.2%.

The results which are summarized in Table I show that the chlorination method is not easily controlled for quantitative estimations. In estimations of this sort it is not to be expected that the results will be concordant to small fractions of a per cent, but the variations observed seem rather too large even for proximate analyses. As stated above, the difficulty of judging the end point of the process was very great. The same treatment did not always yield the same kind of a product, nor show the same percentage of cellulose. If the chlorinations were continued until a perfectly white product was obtained, the percentages were not always alike and seemed to be too low. The results of the ferricyanide reaction did not appear to be of much help.

To assist in clearing up some of these points, we have carried out a series of systematic determinations on four different kinds of wood. Of each kind of wood four (five in the case of No. 1) samples of about five grams were taken. The first sample was boiled in alkaline solution as described above, chlorinated once for one hour, boiled in sulphite solution, treated with permanganate and sulphurous acid, washed and dried; the next sample was treated in precisely the same way except that it had two one hour chlorinations and the accompanying sulphite boilings; and so

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on, each sample receiving one more chlorination than the one before it. In the case of Wood No. 1 the final washings were carried out in the funnel, as in the former experiments, with the other woods the final product was boiled for five minutes in a large volume of distilled water in order to ensure the removal of all reagents. The different kinds of wood, and each of the celluloses, were tested by the ferricyanide reaction. The results are summarized in Table II.

TABLE II

	Color	Per cent. of Cellulose	Per cent. gain by Ferricyanide Reaction
Wood No. 1: Heartwood of Red Spruce.			
Wood		.. .	13.85
Cellulose by 1 chlorination	light brown	61.9	2.52
" " 2 "	light cream	58.5	0.11
" " 3 "	white	51.9	— 1.50
" " 4 "	"	49.1	— 1.55
" " 5 "	"	46.8	— 1.42
Wood No. 2: Sapwood of Red Spruce.			
Wood		.. .	9.51
Cellulose by 1 chlorination	light brown	63.5	6.69
" " 2 "	light cream	53.5	0.79
" " 3 "	white	51.3	— 1.56
" " 4 "	"	47.9	— 2.83
Wood No. 3: Heartwood of Balsam Fir.			
Wood		.. .	11.63
Cellulose by 1 chlorination	light brown	57.3	4.2
" " 2 "	cream	49.4	2.54
" " 3 "	white	44.1	2.02
" " 4 "	"	44.6	1.75
Wood No. 4: Sapwood of Lodgepole Pine.			
Wood		.. .	7.77
Cellulose by 1 chlorination	dark cream	54.6	1.36
" " 2 "	light cream	54.3	1.40
" " 3 "	white	52.3	0.87
" " 4 "	"	49.1	— .10

None of the woods here are very resistant, and in only one case, Balsam Fir, was trouble given by the presence of refractory particles which would not become perfectly white. In all cases when the fiber had received two chlorinations of one hour each, it bleached when again subjected to the action of chlorine gas, instead of turning to the orange-red characteristic of lignocelluloses. Cross and Bevan believe that this orange color with chlorine is a *characteristic* reaction. If that be true, then the complete removal of the lignone complex must take place early during the third chlorination, and the percentage of cellulose falls in between the values found with two and with three chlorinations. The ferricyanide reaction fails to give wholly satisfactory results. We have never been able to obtain a cellulose from wood which does not give

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a blue-green color with this reagent. Why the deep green filtrates should be obtained from some of the tests, and a loss of weight should occur, is not apparent.

The final working out of the following satisfactory analytical procedure was greatly aided by the realization that the end point was indicated by the bleaching of the cellulose in chlorine, and by finding that satisfactory samples could be secured by the use of a wood-worker's rasp.

By holding the wood to be sampled in a vise, and rasping lightly, a finely fibrous sample is readily obtained. The best samples are prepared from green wood; when dry wood is to be sampled, it should be soaked or boiled until thoroughly softened before being rasped. The material is brought to an air dry condition, any large pieces which may perchance be present picked out with forceps, and the very fine particles removed by shaking the air dry sample on cheese cloth or a very fine sieve. The resulting uniform material is then dried at 98°-100°, and 5 gm. portions used for analysis.

The first chlorination should be for one hour; the length of subsequent chlorinations must be to some extent a matter of judgment. If the fiber takes on a very deep orange, showing that a large amount of the lignone is still present, the second chlorination should be for a half or even three quarters of an hour; if lighter colors appear, the time should be shorter. The wood of deciduous trees gives a far paler orange color with chlorine, than that of the coniferous species, and more readily yields a pure cellulose.

The rate of chlorine flow influences the length of exposure required. This is brought out in analyses 1 to 4 in Table III. In analyses 1 and 2 the chlorine was passed in slowly, the first chlorination was not complete, and a second treatment was required. In analysis 3, the gas was passed in more rapidly, and when the fiber was exposed to chlorine the second time it bleached at once. The final result is not influenced, provided the fiber is removed immediately after bleaching occurs. If the cellulose is not removed from the action of chlorine as soon as bleached, it is attacked and a significant loss occurs, as shown in analysis No. 4. When bleaching occurs, the funnel should be transferred to the filter flask, the cellulose treated with water containing a little sodium bi-sulphite to act as an "anti-chlor," then thoroughly washed, transferred to a large size Gooch crucible, and finally washed in the crucible with alcohol and ether. The first part of the drying should be at a gentle heat, ending with a temperature of 98-100°.

Several analyses are given in Table III, all of them satisfactory, except No. 4, where the chlorine was allowed to act on the bleached cellulose.

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TABLE III.

No.	Material	Chlorinations	Per cent. of Cellulose
1	White oak, sapwood	1 hour, 20 minutes and to bleach	55.90
2	" " "	" " " " " "	56.34
3	" " "	and to bleach	56.40
4	" " "	" " "	54.79
5	Red cedar, "	30 minutes and to bleach	42.04
6	" " "	" " " " " "	41.51
7	" " heartwood	" " " " "	42.52
8	" " "	" " " " "	43.00
9	Red spruce "	10 minutes and to bleach	58.95
10	" " "	" " " " " "	58.60
11	Cherry, sapwood	" " and to bleach	54.72
12	" "	" " " "	54.43

The final products were all pure white, and none of them gave the lignin reaction with phloroglucinol and hydrochloric acid.

In conclusion, we desire to acknowledge our indebtedness to Mr. D. C. Parmelee for valuable assistance given us in the analytical work.

FROM THE LABORATORY OF PLANT PHYSIOLOGY,
Sheffield Scientific School of Yale University.

NOTES.

On the Determination of Fluorine.—When fluorine is determined by the Berzelius[1] method the results vary and are considerably too low. Seven determinations gave 76 to 94 per cent. fluorine as calcium fluoride. I repeated the work of Seeman[2] but without being able to find where the loss occurred. Fusing the fluoride with sodium peroxide in a nickle crucible gave no better results. Fourteen determinations, gave 81.4 to 94 per cent. of calcium fluoride taken. I am led to believe that some of the fluorine is retained in the fusion residues as a complex fluoride[3], probably in combination with silica. A. A. KOCH.

MICHIGAN COLLEGE OF MINES,
Houghton, Mich.

The Rapid Determination of Water in Butter. Aluminum Beaker Method.—In the November (1906) Journal,[4] I described a method for the rapid determination of water in butter, of sufficient accuracy for factory purposes, which consisted merely in boiling the water off from a weighed portion of butter contained in a wide test-tube heated by the naked flame of an alcohol lamp. Very shortly thereafter I made a seemingly slight modification in the method, by adopting the use of an aluminum beaker in place of the test-tube—a mere change in utensil, but a change which so greatly improves the method, both by facili-

[1] Pogg. ann. 1, 169; Schweigg. Jsb., 16, 426; and Treadwell: Kurges Lehrbach d. Analyt. Chem., Bd. II, 2te, Auf., p. 326.
[2] Z. Anal. Chem., 44, 369 (1905).
[3] Z. Anal. Chem., 33, 505 (1904); Z. Anorg. Chem., 51, 168 (1906).
[4] This Journal, v. 28, 1611.

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tating its execution and by eliminating the danger of breakage, that it seems worthy of public record.

Another change adopted, following naturally from the first, is the use of a cone-shaped asbestos chimney placed upon the alcohol lamp, to render the flame steady and to render possible the heating of the beaker entirely *over* (instead of partly *in*) the flame, thus avoiding all deposition of soot.

An aluminum beaker of 300 cc. capacity (commonly catalogued as 250 cc.) is used and during the heating is held by a Chaddock clamp or beaker-holder, without rubber covering.

With genuine butters the manipulation is, in a general way, similar to that of the glass tube as described in my former paper; but with renovated butters the beaker is held in a nearly horizontal position, to prevent loss by spattering, and a light glass rod—weighed with the beaker of course—is used for breaking up the lumps of curd that tend to form. In this way the curd is entirely freed of water with little or no discoloration.

Ten grams of butter are sufficient for a charge, and a cream testing balance sensitive to 10 mgms. is sufficiently accurate for the weighing, if protected from air currents.

Following are a few fairly representative results taken from the many I have obtained on both creamery and renovated butters.

Creamery Butters.		Renovated Butters.	
Al. Beaker Method.	Official Method.	Al. Beaker Method.	Official Method.
14.40	14.38	13.20	13.14
13.55	13.32	13.40	13.33
18.60	18.64	16.30	16.25
18.75	18.63	11.30	11.25
12.90	12.97	12.60	12.66
13.40	13.41	16.70	16.55
12.75	12.85	10.40	10.25

G. E. PATRICK.

DAIRY LABORATORY, BUREAU OF CHEMISTRY,
Washington, D. C.
Published by permission of the Secretary of Agriculture.

NEW BOOKS.

THE ELECTROLYTIC DISSOCIATION THEORY. PROF. A. ABEGG. Translated by Dr. Carl von Ende. 180 pages. Price $1.25. Wiley & Sons, New York.

This little book gives a resumé of the electrolyte dissociation theory. The introduction gives the evidences for dissociation in solution, then follows a chapter on equilibria among the ions. Seventy-five pages are devoted to equilibrium among several electrolytes and to hydrolysis. Non-aqueous solutions, influence of temperature and pressure on dissociation and the ionization tendency of the elements make up the last chapters.

We find here the useful and favorable side of the electrolytic dissociation theory presented in a logical order. The serious discrepancy

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between the dissociation of strong electrolytes and the requirements of the law of mass action are considered at the end of the chapter on equlibria among several electrolytes and the various attempts to account for this are given. The idea, that the methods of determining the amount of dissociation are at fault, does not harmonize with the previous attempts to show that the various methods of determining the dissociation give concordant results. The last chapters touch on some of the difficulties encountered by the theory in non-aqueous solutions, many cases of instantaneous reactions are known although the solutions show no measurable conductivities. It is pointed out that the ions have a very great capacity for reaction so only small dissociation is needed and in view of the great influence of water on the rate of a chemcal reaction, it is necessary to show in these cases that this substance is really absent. To the opponents of the theory it is suggested that "we are not accustomed to tearing down a habitable house and putting ourselves out on the street because a few rooms are illy lighted, unless it be we can move into a better one."

As collateral reading for a course of lectures or for students in analytical chemistry this little book should find a place. The equations are developed very simply and the beginner will find here explanations of many things which would otherwise be "rule of thumb." If the beginner lacks a sufficient knowledge of electrochemistry to comprehend some of the points, it is probable that too much detail would cause him to lose interest or miss the main relations. If it appears to some that undue prominence is given to the favorable side of the theory at first, it is to be remembered that this is more or less customary. The beginner learns for example that the volume of a gas is inversely proportional to the pressure to find later that this holds only for restricted domains of a comparatively few gases. The translation seems to have been well done. It is more usual to use the term "cell" than a literal translation of the german "kette."

GEO. A. HULETT.

ELECTROCHEMISTRY. H. DANNEEL. Translated by Dr. E. S. Meriam. 181 pages. Price $1.25. Wiley & Sons, New York.

The author considers that theoretical chemistry and electrochemistry are so intimately related that a knowledge of one presupposes a knowledge of the other. In treating the subject from this standpoint the author has emphasized the fact that the development of electrochemistry has materially affected our chemical theories and that it is an important aid in the investigation of chemical problems.

Work, current and energy are the first subjects treated. Seventy pages are devoted to a consideration of chemical equilibrium, the theory of electrolytic dissociation and conductivity. The treatment of these subjects is necessarily brief. The beginner must take much for granted, particularly in the development of equations, but there is here a good review for the

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more advanced. With this foundation the author has given the essential features of electromotive force, galvanic current,, polarization and electrolysis, in a compact and connected form. This makes a readable little book which should find a place among our electrochemical textbooks.

The derivation of the gas equation from the laws of Boyle's and Gay Lussac (p. 17-18) should be either more complete or only the final result given. The equation $pv = p_0 v_0 (1 + at)$ is not the product of the two equations given. The combination of the two laws depends on a proposition in variations and it might not be out of place to state this proposition in chemical text books for then the derivation is direct and simple and avoids the usual cumbersome, and generally to the beginner, misleading derivation. On page 79 and 81 the term "specific conductivity" is used, where no doubt specific conductance was intended. GEO. A. HULETT.

THE PRINCIPLES OF QUALITATIVE ANALYSIS, FROM THE STANDPOINT OF THE THEORY OF ELECTROLYTIC DISSOCIATION AND THE LAW OF MASS ACTION. BY WILHELM BÖTTGER, Privat-docent in the University of Leipzig. Translated with the author's sanction and revised with his co-operation by William Smeaton, Instructor in General Chemistry in the University of Michigan. Price $2.00. Pp. 300 and XVI. P. Blakiston's Son & Co., Philadelphia, 1906.

The treatment of Qualitative Analysis from the point of view of the application of the equilibrium law to its reactions, as first demanded by Ostwald, appears now indispensable for a thorough comprehension of its methods and consequently for an intelligent completion of an analysis. On the other hand Qualitative Analysis affords splendid material, from a purely pedagogical point of view, for making a student thoroughly familiar with the application of these fundamental laws of chemistry to the most varied chemical changes; there is quite a difference between learning such laws and knowing how and where to apply them in the complex phenomena of most chemical changes. The study of analysis from the point of view mentioned has therefore the twofold advantage of developing keener, more intelligent analysts, and of developing better chemists through analysis. In Böttger's Qualitative Analysis, we have a very laudable effort to present the subject thoroughly and consistently from this point of view and without detriment to the purely analytical value of the book. For the trained, mature chemist and analyst, it is full of sound, interesting material and discussions. But it seems to the writer that pedagogically the treatment has been carried out in an extremely weak and confusing way and that this book in the hands of beginners in analysis would rather confuse than help them. There is no need at all for such an effect, for the treatment from the physico-chemical standpoint can be made pedagogically, simple, logical, direct and convincing. We note for instance that the treatment of complex ions (p. 16) precedes the presentation and application of the mass-action law (p. 33) and thus has become practically un-

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intelligible to a beginner, who is plunged *ab initio* into a subject which he really cannot understand without the application of this law, by means of which the whole subject may be made beautifully clear and simple.

From the purely analytical point of view, the most interesting contribution by Böttger is the use of a systematic grouping of anions through the solubilities of the barium, lead and silver salts. For those who still favor the converting of the acids into soluble alkali salts as preliminary to the acid analysis, this grouping will probably prove welcome. In the experience of the writer, the change into alkali salts is subject to so many complications and exceptions and the gain by such a grouping is often so small, that it has been discarded except for the so-called "insoluble" (in acid) unknowns and all tests for acids, group and individual, are now carried out in *acid* solutions, without removing the cathions: most of the important acid tests are, as it is, carried out in acid solutions and the results of the analysis for metal ions, with the solubilitites of solid unknowns and the reaction of solutions, will usually give very considerable information as to what groups of acids may be present.

JULIUS STIEGLITZ.

UNIVERSITY OF CHICAGO.

PRACTICAL PHYSIOLOGICAL CHEMISTRY. By PHILIP B. HAWK, Demonstrator of Physiological Chemistry in the Department of Medicine of the University of Pennsylvania. pp. 416. Price $4.00 net. P. Blakiston's Son & Co., Phila.

This book is a combination of a laboratory manual and a text book. Attention is given in the main to the practical side of the subject but enough facts are introduced to make the outlined experiments intelligible. A new feature that has been introduced is a detailed study of the feces. One of the best points connected with this volume is the large number of beautiful illustrations of crystals and various pieces of apparatus.

F. P. UNDERHILL.

AUSFÜHRLICHES LEHRBUCH DER PHARMAZEUTISCHEN CHEMIE, BEARBEITET VON DR. ERNST SCHMIDT, Ordent Professor der Pharmazeutischen Chemie und Director der Pharmazeutischen-Chemischen Instituts der Universität, Marburg-Erster Band, Anorganische Chemie, Erste Abteilung; Mettalloide Fünfte vermehote Auflage. Viewig u. Sohn, Braunschweig, 1906. pp. 528. Ladenpreis: geheftet Mark 10.

For years past this book has occupied a unique place as a treatise on chemistry and although entitled Pharmaceutical Chemistry and containing much that is useful to the pharmacist it is really a book of the greatest value to chemists in general. As a book of reference it is of especial value as it contains a vast amount of information and is somewhat unique in that not a little part of the information is of the uncommon sort that one is not apt to find included in a single book. The part under review is the first section of the first volume of the fifth edition which comprises the

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metalloids. The sections that are to follow will doubtless be of equal excellence. JOHN MARSHALL.

FOODS AND THEIR ADULTERATION. Origin, Manufacture and Composition of Food Products. Description of Common Adulteration, Food Standards, and National Food Laws and Regulations. By HARVEY W. WILEY, M.D., Ph.D. Price $4.00. Octavo, 625 pages. P. Blakiston's Sons & Co., Philadelphia.

With the widespread interest given to Foods, not alone by the scientists and manufacturers and distributors, but also by the legislators and consumers, no time is more appropriate for the appearance of an authentic manual on this subject, than the present. It is fortunate for the American consumers that a treatise has appeared, written by such a well known and highly recognized authority as Dr. Harvey W. Wiley, Chief of the Bureau of Chemistry, U. S. Department of Agriculture.

Dr. Wiley divides his subject matter into three classes:—Foods, beverages and condiments. Foods and condiments are considered only in this the first volume, and beverages will be taken up in the second volume, now in active preparation. Milk is included among the foods, as the author very correctly states: "Milk, although a liquid substance, is hardly to be considered a beverage, and on account of its high properties may be classed, together with its preparations, under the first head."

Analytical chemical methods and detailed figures of analyses are intentionally omitted, although in every case the average chemical composition of each class is given. This is a distinct advantage, making the manual more concise, especially also as the manual is designed—"to interest the consumer, as well as the manufacturer, the scientific, as well as the general reader."

The different products are treated under the following sub-divisions: Introduction: A brief outline of Proper Ration, Social Function of Food, Definition, Composition and Classification, and Explanation of some of the more Common Chemical Terms.

Part 1—Meats and Meat Products.
Part 2—Poultry and Eggs and Game Birds.
Part 3—Fish Foods.
Part 4—Milk and Milk Products and Oleomargarine.
Part 5—Cereal Foods.
Part 6—Vegetables, Condiments, Fruits.
Part 7—Vegetable Oils and Fats, and Nuts.
Part 8—Fungi as Foods.
Part 9—Sugar, Sirup, Confectionery, and Honey.
Part 10—Infants' and Invalids' Foods.

The space allowed the reviewer is too limited to allow him to go into detail as to any part of this excellent manual. Every part is written in the characteristic plain and forcible style of the author, showing complete

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mastery of the subject and based on the very extensive personal experience of Dr. Wiley. All opinions and conclusions drawn "respecting adulterations, misbranding, nutritive value, and wholesomeness are the individual expressions of the author and are not to be considered in any other manner." A necessary, although perhaps not required explanation, on account of the official position that Dr. Wiley holds.

The reviewer cannot agree with the author "that the inartistic treatment of a subject of this kind, is not one which is calculated to excite any sympathetic interest or appeal to the natural desire for literary and artistic expression." The literary style is such that both scientist and layman are liable to try to finish the manual from "cover to cover" at one reading. The artistic make up is excellent throughout, as to type, tables and illustrations and the book is exceptionally free from errors or imperfections. The Table of Contents, Index and List of Illustrations (11 colored plates and 86 others) are complete and splendidly arranged.

The reviewer has no hesitation in stating that this latest manual from the pen of Dr. Harvey W. Wiley is one of the best scientific and popular additions to food literature, and that it can be recommended without qualfication, not alone to the specialist interested in the manufacture, distribution or control of food products, but also to the physician, sanitarian, legislator and to every consumer of food products.

EDWARD GUDEMAN.

GLUE AND GELATINE. THE PRACTICAL TREATISE ON METHODS OF TESTING AND USE. BY R. LIVINGSTON FERNBACH. pp. IX + 208. Price $3.00. D. Van Nostrand & Co.

This book presents to us the most practical treatise from the chemical technological point of view that has as yet been published.

The author takes up the nature, properties and sources of various kinds of commercial glues and their manufacture. He next examines them from a physical point of view and gives the tests and classification thus derived. He then examines them in a chemical way and it must be admitted that when a conservative author only gives us moisture, ash, acidity, alkalinity, acids and fats as the well established chemical methods of valuation, which have little value as a qualitative factor, then it must be acknowledged that the subject is difficult.

Mr. Fernbach starts his third chapter; "It must be reaffirmed at the outset that analysis supplies no data as to the strength of the product." The methods offered for the approximate assay of constituent elements and the estimation of glue content, can hardly be called chemical methods, but they are the best we have.

In his chapter on adulteration, he has followed Allen very closely from a chemical standpoint, bearing in mind the necessity of having his method clear and concise on each subject. The whole value of this work to chem-

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ists who have glue analyses to make, is the position the author takes that the physical tests must determine the value of the glues and there can be no question but that the author proves his thesis.

Much credit is given the standards of physical tests, known as "Cooper grades," which depend greatly on the viscosity and jelly strength—by the latter is meant the resistance to pressure of a given glue when compared with other glues of known character.

His book should be in the hands of all chemists who have glue work to do and comes nearer to being a hand-book of the subject than anything yet printed, giving as it does all the chemical and physical tests of value and entering also largely into the commercial side of the subject.

JOHN H. YOCUM.

"THE PEABODY ATLAS."—SHIPPING MINES AND COAL RAILROADS OF THE CENTRAL COMMERCIAL DISTRICT OF THE UNITED STATES. Accompanied by Chemical, Geological and Engineering Data. By A. BEAMENT. Price $5.00. 149 pp., size 16¾ x 18 in. Peabody Coal Co., Chicago. 1906.

This is an exceedingly valuable compilation of coal information and represents a vast amount of labor as well as great expense. Three general maps of the United States are given with especial designations of coal fields. Twenty-five sectional maps 14"x16" give counties, railways, and mines in detail, the latter numbered for ready reference to the lists of coal, localities, coal operators and coal railroads arranged alphabetically under each head. The statistical and geological data are concise and well arranged. Not the least valuable feature is a well illustrated description of the author's theories concerning the combustion of coal under the heading of "Smokeless Furnaces and Smoke Suppression." Few writers are so well qualified to discuss this and related topics where fuel of the bituminous type is involved.

S. W. PARR.

WATER SOFTENING AND TREATMENT. WILLIAM H. BOOTH. 8vo., pp. XVI + 308. Price, $2.50. D. Van Nostrand & Co., New York, 1906.

The literature in English upon boiler waters is meagre. Real contributions, therefore, to our information on this topic are welcome. Thirty pages are devoted to a discussion of the mineral constituents and reactions of possible reagents. The author is evidently an engineer rather than a chemist, and most of the chemical data are "said to be" as given in the text. This second hand characteristic of the descriptive matter probably accounts for the lack of discrimination in the topics introduced. Magnesium hydrate, for example, may be interesting, but hardly practical, while no mention is made of phosphates as reagents. The discussion of analytical methods covers six pages and is devoted solely to a description of the use of soap solutions. A more pretentious discussion along these lines is contained in Appendix No. 1, covering sixteen pages. This

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is a reprint of Dr. Angus Smith's report on the Incrustation in Boilers near Manchester, England, first printed in 1859 and repeated here with the chemical nomenclature in the old style.

Nearly one-half of the book is taken up with a description of condensers, feed heaters and feed pumps, pp. 149-288. Fifty pages are devoted to a description of water softening apparatus common to England and the Continent. No American types are referred to. The book may not be without interest to the engineer, but has little of value for the chemist.

S. W. PARR.

SCIENTIFIC ASPECTS OF WATER PURIFICATION. BY FREELAND HOWE. 8vo, pp. 53. Pittsburgh Filter Mfg. Co., 1906.

In the preface, the author states that "the writer's principal desire is to present to others the ideas which make water purification more comprehensible and simple to him." It is possibly comprehensible that one may dwell so persistently among the ions as to be able to make truthfully such a statement as the one quoted, but to the ordinary individual, the descriptive matter of this little treatise will seem to give the rather simple problems of water purification a most terrific twist to bring them into the "scientific aspect" of the author. One example may be cited as illustrative of the general plan of "simplification." The familiar reaction of Prof. Clark for the softening of water is put thus: "If an increase of a solid phase in contact with the system resulted in the increase in concentration of one of the ions, when the system was already saturated with respect to that ion, there would be a change. The point of saturation would be reached and the solid phase of the least soluble of the components would separate out. This is what happens when lime is added to a system containing the ions, carbanion (CO_3''), hydro-carbanion (HCO_3') and the calcion (Ca'') and magnesium (Mg'')." The author states that "all the salts are in a state of electrolytic dissociation . . . each chemical or group of elements exists as ions or atoms with charges of either positive or negative electricity he discusses as illustrations, hydrion, diferrion, triferrion, etc., but does not say anything about silicon. Any discussion of quantivalent reactions seems to be avoided. This would require distribution of ions in conformity with the every day conceptions of the compounds involved. The nearest approach is in the following paragraph taken from page 32. "Sulphanion can be almost completely removed by supplying barion . . . It is rendered non-scale forming by supplying it with sodium or potassium, but the resulting sulphates of sodium and potassium causes foaming." It is difficult to determine whether the last clause is a lapse or a concession. In general here is another illustration of a fine system put to bad service. If the work is intended as a dissertation on physical chemistry, it would seem that an un-

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fortunate topic illustrative of that subject had been chosen. It can hardly be taken seriously as an elucidation of the facts pertaining to water softening, except in those parts where elaborate quotations (Thirteen pages) are made from Handy, Cairns, Fresenius, Kennicott, Campbell, etc.

S. W. PARR.

WATER FILTRATION AND ITS RELATION TO MUNICIPAL HEALTH AND PROSPERITY. F. B. LEOPOLD. 29 pp. Pittsburgh Filter Mfg. Co.

This pamphlet well illustrates the quotation made in the introduction that "It is better to fence the precipice at the top than wait with an ambulance at the bottom." A brief review of the principal typhoid epidemics is given. Plymouth, Pa., Grand Forks, N. D., Ithaca, N. Y., Butler, Pa., and Columbus, O., together with very convincing evidence as to the efficiency of properly devised and conducted filtration plants. The increasing necessity for safe-guarding water supplies makes this brief discussion timely and valuable.

S. W. PARR.

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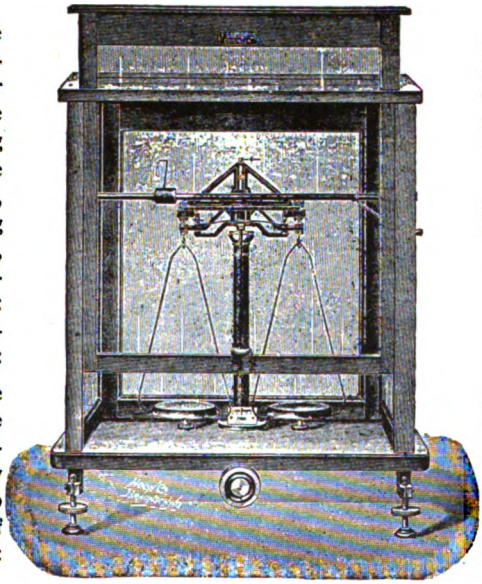
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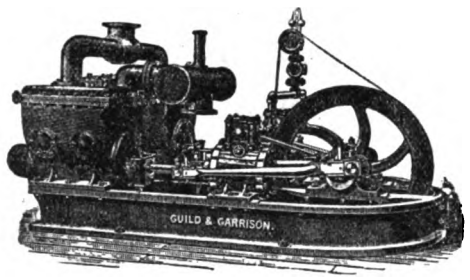
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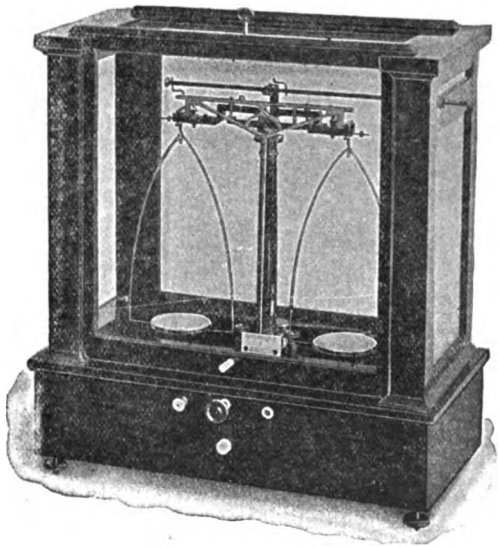
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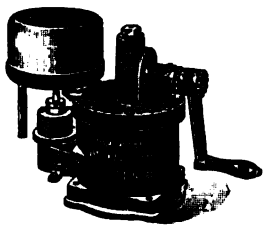
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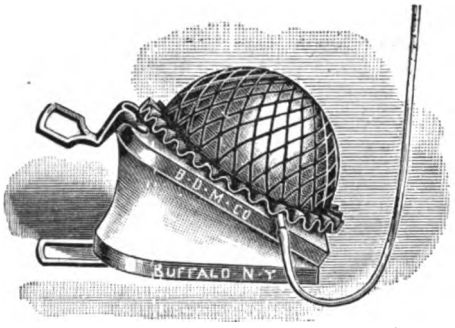
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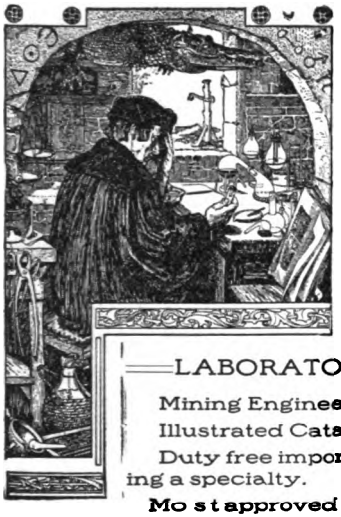
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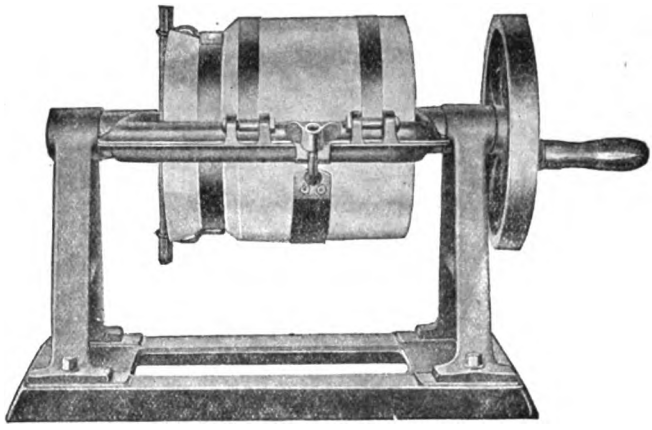
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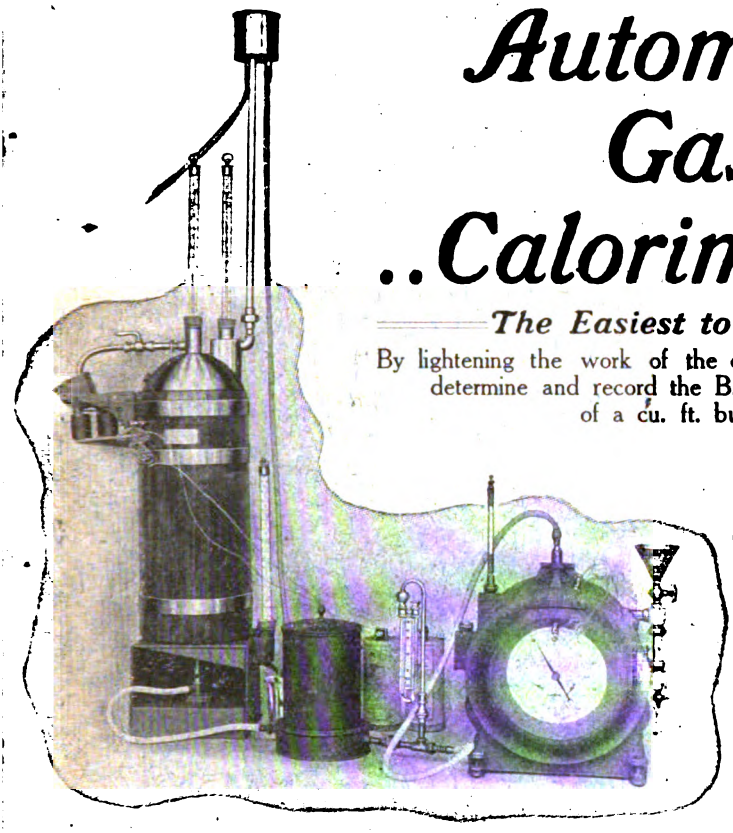
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THE JOURNAL

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DECOMPOSITION OF HYDRATED AMMONIUM SALTS.

BY WILLIAM M. DEHN AND EDWARD O. HEUSE.

Received May 31, 1907.

Under the influence of rising temperatures, diammonium oxalate[1] decomposes as follows:

I.[1] $(COONH_4)_2.H_2O = (COONH_4)_2 + H_2O$

II.[2] $(COONH_4)_2.H_2O = (COOH)_2 + H_2O + 2NH_3$

III.[3] $(COONH_4)_2.H_2O = HCOOH + CO_2 + 2NH_3 + H_2O$

IV.[4] $(COONH_4)_2.H_2O = (CONH_2)_2 + 3H_2O$

V.[5] $(COONH_4)_2.H_2O = CO_2 + CO + 2NH_3 + 2H_2O$

VI.[6] $(COONH_4)_2.H_2O = HCN + CO_2 + NH_3 + 3H_2O$

VII.[7] $(COONH_4)_2.H_2O = C_2N_2 + 5H_2O$

Some of these reactions take place at approximately the same temperatures; others only at successively higher temperatures. That equation I represents the initial decomposition is established with certainty[1]; the end-products at high temperature are shown to be largely cyanogen and water. It was observed that only equations I and II represent reversible reactions which are rapid and complete; the products of reaction III condense to ammonium formate and ammonium bicarbonate; some of the products of reaction V and VI condense to ammonium carbonate and ammonium bicarbonate; reaction IV and VII[8] are practically non-reversible.

[1] Dupre, Analyst, 30, 266; Ber., 18, 1394; Gillot, Bull. Acad. Roy. Belg., 1900, 744.

[2] Gillot; Gay Lussac, Ann. chim. phys., 46, 218.

[3] Turner, Schweigg, Jour. 62, 444; Pogg. Ann., 24, 166. Dumas, Ann. chim. phys., 44, 129 (1830).

[4] Ibid, 54, 240.

[5] Dumas; Gay Lussac; Lorin, Compt. rend., 82, 750.

[6] Dumas.

[7] Dumas; Michael, Ber. 28, 1632.

[8] Peleuse and Richardson (Ann. 26, 63) show that water and cyanogen yield ammonium oxalate. Zellet (Monatshefte 14, 224) finds that when cyanogen is heated with water at 100°, he obtains oxalic, hydrocyanic and azulmic acids, urea, carbon dioxide, and ammonia.

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From consideration not only of the number of these possible reactions but also of the diversity of the products formed, it may be supposed that the decomposition of this simple salt involves a hopeless complexity; however, the following studies seem to indicate that the order of successive decompositions is largely as shown in the equations:

$$(COONH_4)_2.H_2O = (COONH_4)_2 + H_2O$$
$$(COONH_4)_2 = (CONH_2)_2 + 2H_2O$$
$$(CONH_2)_2 = C_2N_2 + 2H_2O$$

Samples of pure diammonium oxalate in open crucibles were heated in air baths whose temperatures were held constant during one hour. The total loss in weight and the residual ammonia were determined in each experiment with the following results:

Experiment	Temperature	Loss per cent of		
		Total	Ammonia	Water[1]
1	80°	9.51		9.51
2	95°	12.17		12.17
3	118°	13.17		13.17
4	143°	14.02		14.02
5	153°	15.42	0.33	15.09
6	168°	63.78	6.75	56.03
7	178°	78.65	13.86	64.73
8	193°	87.89	13.92	74.03
9	243°	89.21	18.95	70.26

These experiments show that when dry diammonium oxalate is heated:

1. It evolves one molecule of water below 100°[2] (Equation 1); and, to 150° at least, decomposes according to Equation IV.

2. Below 168° the loss of water is even greater than that represented by equation IV (38.02 per cent.); hence oxamide is largely formed at these temperatures.

3. At 150° ammonia begins[3] to be evolved (Equation II) and at higher temperatures it continues to be evolved or else the substance sublimes.

Since oxamide sublimes but, as shown below, does not decompose into cyanogen and water (Equation VII) below 280°, it may be concluded that the lower temperatures represent only two main decompositions (I and IV). Efforts were made to confirm this by vapor pressure curves.

[1] And other products at higher temperature; the total per cent. of water is 63.37 per cent.

[2] One molecule of water represents 12.67 per cent.

[3] Gillot (*J. Chem. Soc.*, 1901, A 118) shows that ammonia is completely hydrolyzed and expelled from boiling solutions of diammonium oxalate.

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VAPOR PRESSURES OF DIAMMONIUM OXALATE.

Temp.	Pressure	Temp.	Pressure
71	11	145	2134
74	19	156	2748
82	53	161	3144
85	58	168	3877
90	72	171	4319
95	78	176	4821
98	85	180	5233
111	314	182	5546
121	597	187	6084
122	827	195	7103
126	999	197	7326
131	1271	200	7682
138	1616	205	8219
141	1815	210	8818

VAPOR PRESSURES OF OXAMIDE.

Temp.	Pressure	Temp.	Pressure
265[1]	45	293	1596
270	71	294	1911
274	86	294.5	2115
277	118	295	2157
283	241	295.5	2301
290	278	296.5	2412
291	1182	297	2536
292	1383	297.5	2752[2]

It will be observed that the vapor pressure curve of diammonium oxalate is represented by three distinct segments. Segment A unquestionably represents the partial aqueous decomposition; segment B evidently represents the elimination of the molecule of water of crystallization (equation I); and segment C represents the decomposition into oxamide and probably the simultaneous decomposition represented by equation II, III, V and VI. That reaction VII does not take place below 290° is sufficiently indicated by the curve of oxamide.

Monoammonium Oxalate.

This salt, prepared by the methods of Nichols[3] and Walden[4], was found to be pure $NH_4HC_2H_4.H_2O$. It is reported that when heated, this salt is stable to 70° ; at higher temperatures, it begins to lose its water of crystallization[5]; at 140° it forms oxamic acid[6]; at more elevated temperatures, it yields carbon dioxide, carbon monoxide, formic acid and oxamide ; finally, it expels hydrocyanic acid and ammonium carbonate; the residue contains oxamic acid and oximide .

When samples of the salt were heated in open crucibles in the manner indicated above, the following data were obtained:

[1] Sublimation was observed at this temperature.

[2] The non-reversible pressure was equal to 1182 mm.; a large quantity of cyanogen was found.

[3] Chem. News, 22, 14.

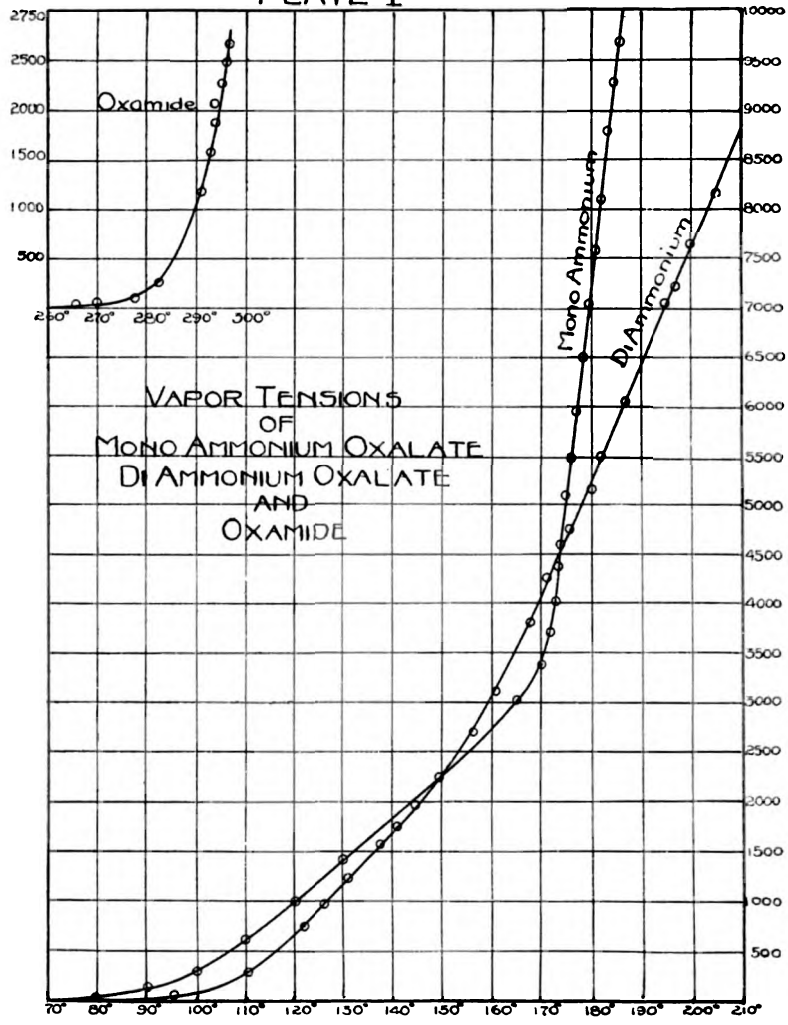
[4] Am. Ch. J., 34, 147.

[5] Balard, Ann. chim. phys., (3) 4, 94; Ann., 42, 197.

[6] Ost. and Mente, Ber., 19, 3229.

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PLATE I



Experiment	Temperature	Loss per cent. of		
		Total	Ammonia	Water
1	75	. . .	. . .	. . .
2	94	2.68	. . .	2.68
3	105	7.47	. . .	7.47
4	115	8.54	. . .	8.54
5	134	9.09	0.13	8.96
6	155	10.99	0.30	10.69
7	169	11.51	1.03	11.48
8	183	48.36	1.71	46.65
9	200	88.51	8.98	79.53
10	225	99.64	12.24	87.40

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It is seen that monoammonium oxalate:

1. Is stable to 75°,

2. Parts with its molecule of water of crystallization (14.40 per cent.) below 170°.

3. Loses two other molecules of water at 183° and simultaneously incurs a secondary decomposition or *sublimes*.

Therefore the main successive decompositions are probably indicated by the equations:

$$NH_4HC_2O_4.H_2O = NH_4HC_2O_4 + H_2O$$

$$NH_4HC_2O_4 = HOOCCONH_2 + H_2O$$

$$HOOCCONH_2 = \begin{matrix} CO \\ | \\ CO \end{matrix}\!\!>\!NH + H_2O$$

The above data of decomposition are closely confirmed by the vapor pressures of the substance.

Temperature	Pressure	Temperature	Pressure
81	7.7	145	2131
88	15.9	150	2370
95.8	50.2	155	2682
106	469	160	2964
110	686	165	3096
115	875	170	3268
122	1102	175	4009
125	1230	176	5862
130	1420	180	7427
135	1623	182	8159
140	1840	185	9846

It will be observed (see plate 1) that (1) the general form of the two curves are much alike, (2) the molecule of water in each salt is completely eliminated below 100-170°, and (3) the upper segments represent the second stages of decomposition.

Decompositions of the above organic compounds indicate that the initial and predominating reactions involve the expulsion of water; and that simultaneously, particularly at higher temperatures, secondary reactions indicated by the dissociation of ammonia, are involved. It was hoped that studies of inorganic hydrated ammonium salts, along the lines indicated above, would lead to a more intimate knowledge of water of crystallization and of the structure of hydrated salts. That this hope has been partially realized is evidenced by the following studies.

It was found, for instance, that certain hydrated ammonium salts decompose so as to yield both water and ammonia at most temperatures above the initial temperature of decomposition. Studies of the *rate* of expulsion of water and ammonia have shown that abundant yields of ammonia usually accompany the largest yields of water; and, though the last trace of ammonia is given off only with the last trace of water, it is given off simultaneously with it at most of the lower temperatures. In

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other words, curves of expulsion of ammonia, as well as of water, extend from the temperatures of initial decomposition to those of complete decomposition; consequently tracing the course of ammonia through the *composite* decompositions leads to knowledge of the respective individual decompositions and, as will be shown, throws light upon individual structures in the complete structure. For instance, suppose it can be shown that highly polyhydrated ammonium salts are largely decomposed below 100°, while the residues of ammonia and of "water of composition" are completely expelled only at considerably higher temperatures, it may then be concluded that *the union of ammonia resembles more closely the union of "water of composition" than the union of "water of crystallization."* Again suppose it can be shown that ammonia is given off at all lower temperatures; it may also be concluded that *both "water of crystallization" and "water of composition" are given off at all of these lower temperatures.*

In respect to the methods used to differentiate the respective dissociations, it has been found that vapor pressure curves (*vide plate VII*) are not necessarily indicative of the *qualitative* decompositions of compounds; in the case of polyhydrated salts they are a measurement only of the *composite* effect of a number of co-temporaneous dissociations. For instance if each molecule of water and ammonia in the original compound has a definite vapor pressure for each temperature, it may easily be seen that the resultants of their pressures may so blend as to indicate no definite breaks in the vapor pressure curve, therefore, *recognition of points of decomposition may fail entirely when only vapor pressure curves are studied.* For this reason other methods of investigation have been employed.

Decomposition of Inorganic Salts.

Various investigators[1] have represented partially dehydrated salts, for instance, hydrated ammonium salts, by very contradictory and, as shown below, by very erroneous formulas. We find in the periodicals and the text-books that free use is made of formulas:

$$(NH_4MgAsO_4)_2.H_2O \text{ and } (NH_4MgPO_4)_2.H_2O$$

to represent ammonium magnesium arsenate and ammonium magnesium phosphate dehydrated at 100-110°: Though most investigators agree that the composition of ammonium magnesium arsenate at ordinary temperature is $NH_4MgAsO_4 6H_2O$, a considerable difference of opinion as to its composition at temperatures between 98° and 100° is expressed. For instance Bunsen[2] concludes that nearly ½ of a molecule of water is held at 98°. Rose[3], Puller[4], Field[5], and Lefevre[6], affirm that exactly ½ mol. H_2O is retained

[1] Wach, Schweigger's J. Chem. Physik, 59, 288; Rose, Z. anal. Chem., 1, 417; Ann. Physik., 76, 20; Z. anorg. Chem., 23, 146. Puller, Z. anal. Chem., 10, 68.
[2] Ann. Pharm., 192, 311.
[3] Z. anal. Chem., 1, 417.
[4] Ibid, 10, 68.
[5] Jahrsb., 1858, 170.
[6] Ann. chim. phys., (6) 27, 55.

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by the salt when it is dried at 100° on the water bath; Fuller holds that it is practically dehydrated at 103°; and Bunsen[1] further states that is completely dehydrated at 104.5°. These data do not appear to be particularly discordant; but in view of the fact, as shown in this research, that 3-4 per cent. of ammonia—equivalent in weight to about ½ mol. H_2O—are lost at these temperatures, none of the conclusions drawn are correct. For when the salt is dried at these temperatures less ammonia and more water are present than are represented by the formula $(NH_4MgAsO_4)_2.H_2O$. A more correct representation would be a mixture in equal proportions of $HMgAsO_4.H_2O$ and $NH_4MgAsO_4.H_2O$. However, even this formulation will be shown to be incorrect, for one conclusion of these studies is that *no definite formula can be given to many hydrated ammonium salts dried at temperatures between 40°-200°*.

This is clearly illustrated by data obtained on heating samples of these salts at definite intervals of temperature for equal lengths of time and determining both the total loss in weight sustained and also the weight of ammonia evolved. The salts, contained and weighed in U-shaped tubes, were heated in baths controlled by thermostats, while air, dried and freed from carbon dioxide, was passed continuously through the tubes and into flasks containing standard sulphuric acid. The total loss of weight in the U-tubes represented, of course, the loss of both water and ammonia; this weight, less than the weight of ammonia, determined by titration, gave the loss of water.

It was found that quite different results were obtained when we varied the following conditions: 1. Temperature. 2. Time. 3. Kind of drying gas. 4. Quantity of drying gas. 5. Size of salt crystals. 6. Preservation of salt crystals. 7. Manner of heating.

The effect of temperature is the most important and it was on temperature as a basis that the following studies were made.

The influence of time was soon found to be a very disturbing factor, for these salts do not dry to definite composition, therefore briefer or longer desiccation gave very widely different per cents. of decomposition.

This is seen in the following table:

Substance	Weight	Loss	Loss per cent.	Time	Temp.
$NH_4MgPO_4.6H_2O$	0.7473	0.0423	5.66	4	70°
$NH_4MgPO_4.6H_2O$	0.4636	0.1658	35.76	40	70°
$HNaNH_4PO_4.4H_2O$	0.8016	0.1178	14.70	4	76°
$HNaNH_4PO_4.4H_2O$	4.7094	1.0784	22.89	57	75°
$NH_4MgAsO_4.6H_2O$	0.7941	0.0136	0.35	4	50°
$NH_4MgAsO_4.6H_2O$	0.7958	0.0372	4.67	20	50°
$NH_4MgAsO_4.6H_2O$	0.2920	0.1108	37.95	4	110°
$NH_4MgAsO_4.6H_2O$	1.1127	0.4556	39.61	40	110°

It will be observed here that heating for four hours invariably gave lower per cents. of decomposition than when heating for 20-57 hours. An ex-

[1] loc. cit.

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planation of these great differences of results on short and protracted heating is conceivable when one recalls that "water of crystallization" is more easily expelled than "water of composition". The former is usually eliminated at temperatures below 100°; the latter, at temperatures above 100°. By protracted heating at low temperatures, however, "water of composition" may be removed completely, therefore too prolonged heating at low temperature does not reveal the normal decomposition at these temperatures. On the other hand too brief a heating at low temperatures does not insure complete removal of the decomposition products. It was to avoid on the one hand incomplete dehydration, and on the other excessive secondary decomposition that periods of 4–7 hours heating were finally chosen.

It was found, moreover, that heating the salts progressively, that is heating the same sample to successively higher temperatures, did not yield the proper results, for, on comparing the per cents. of decomposition obtained by heating different samples at the respective temperatures, very different results were obtained.

The method of heating individual samples at different temperatures for the same lengths of time was adopted, in preference to heating the same sample successively to higher temperatures, for the reason that the former method really eliminates the element of time and thus minimizes secondary decompositions. For instance when a sample of a salt is heated at 65° for four hours and then another sample of the same salt is heated at 70° for four hours, all other conditions remaining the same, the difference of effect is the result of temperature alone. A further reason for employing the method of separate samples for each interval of temperature, was to avoid the accumulative errors of analysis involved in the other method.

The effect of using different gases to carry off the decomposition products may be seen in the use of hydrogen and of air. In the following table, the data were obtained on heating microcosmic salt for periods of four hours each.

Temperature	Per cent.	Carrier
50°	0.35	Hydrogen
50°	0.60	Air
50°	0.59	Air
76°	9.64	Hydrogen
75°	16.35	Air

The results here indicate that hydrogen is not so efficient a carrier as air, and this undoubtedly is owing to the fact that it possesses a much more rapid rate of diffusion.

The effect of *speed*, or rather the quantity, of carrying gas, is seen in the following experiment. Dry air was passed for 27 hours over 4.4334 grams of $NH_4MgAsO_4.6H_2O$; it lost 0.2114 grams or 4.89 per cent.

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whereas another sample of 3.4729 grams exposed to quiet air for the same time lost scarcely a weighable quantity.

The air used in the following experiments was regulated so that 60–70 bubbles per minute passed from the exit-tube dipping into the flasks containing the standard acid. At first considerable difficulty was encountered in regulating this passage of air but after a number of trials the following, quite satisfactory system was adopted. The air from the main supply was passed through a bottle connected on the one hand with the drying-train and on the other with a shunt tube dipping into a definite depth of water. The object of the shunt was to force through the drying system air backed by a constant pressure, equal always to the height of water in the shunt system when air was constantly passing out of the latter. The quantity of air passing through the drying system was controlled by a screw clamp attached to a rubber tube in connection with the exit tube. By this means the number of bubbles per minute could be regulated to a nicety ; the size of the bubbles passing through the normal sulphuric acid, was limited, of course, by the size of the exit tube dipping into it.

Fifthly, the size of the salt crystals used was found to exercise a very appreciable effect on the results ; mass varying as the cube, and radiating surfaces as the square of the diameter. To reduce this influence to a minimum the crystals were pulverized so as to pass through a particular, fine-mesh sieve.

Sixthly, efflorescence of some salts, for instance with ammonium calcium arsenate, was found to introduce large factors of error. The weathering, that is the decomposition of these salts at ordinary temperature, is often so great, particularly in summer, that only freshly prepared samples could be used.

Finally, the manner of heating, for instance, whether in open crucible, in desiccators over sulphuric acid, or in the U tubes mentioned above, was found to yield different per cents. of decomposition. Of course the same method of heating was employed throughout any given experiment, nevertheless at some temperatures certain abnormal results were often obtained and can be explained only on the basis of "suspended transformation". For instance in the following table :

Substance	Temperature	Per cent. volatilized
$Al_2(SO_4)_3.18H_2O$	83.0	11.79
"	90.5	4.69
$KAl(SO_4)_2.12H_2O$	71.5	8.35
"	83.0	2.21

it is seen that higher temperatures yield lower per cents. of decomposition though the experiments were carried out under similar conditions. Heating *at once* to the higher temperatures seems to induce this "suspended transformation."[1]

[1] See page 1161.

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Though recognizing the above mentioned influences and observing in the experiments every precaution necessary to avoid their disturbing effects, concordant results were often obtained only after repeated trials. This difficulty of obtaining concordant results was particularly noticeable at temperatures at which more than one molecule of water was given off, for instance in the case of ammonium magnesium arsenate, at 70–90°.

The following table includes data obtained in studying the decomposition of ammonium magnesium arsenate prepared in the usual manner and found by analysis to be strictly $NH_4MgAsO_4.6H_2O$.

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII[1]
Temperature	Weight salt	Loss of weight of			Ratio of	Total per cent. loss of			Fractional per cent. loss of		
		H_2O+NH_3	NH_3	H_2O	Both	H_2O+NH_3	NH_3	H_2O	H_2O+NH_3	NH_3	H_2O
40	0.7752	.0008	.0002	.0006	4.0	0.10	0.02	0.08	0.10	0.02	0.08
45	1.0344	.0030	.0003	.0027	9.0	0.29	0.03	0.26	0.19	0.01	0.18
50	0.2692	.0042	.0003	.0039	13.0	1.56	0.11	1.45	1.27	0.08	1.19
56	0.2875	.0053	.0005	.0053	10.6	2.01	0.17	1.84	0.45	0.07	0.38
60	0.6945	.0264	.0027	.0237	8.8	3.80	0.39	3.41	1.79	0.22	1.57
65	0.6482	.0629	.0063	.0566	8.9	9.70	0.97	8.73	5.90	0.58	5.32
70	0.8108	.0828	.0093	.0735	8.0	10.21	1.15	9.06	0.51	0.18	0.33
75	0.2698	.0343	.0039	.0304	7.8	12.71	1.34	11.37	2.50	0.19	2.31
75	0.2332	.0379	.0038	.0341	8.9	16.35	1.72	14.63	3.64	0.38	3.26
80	0.5166	.1563	.0164	.1399	8.5	30.26	3.18	27.08	13.91	1.46	12.45
82	0.2402	.0832	.0087	.0745	8.5	34.64	3.63	31.01	4.38	0.45	3.93
85	0.3164	.1162	.0122	.1140	8.5	36.72	3.86	32.86	2.08	0.13	1.95
100	0.3247	.1212	.0127	.1085	8.6	37.31	3.90	33.41	0.59	0.04	0.55
110	0.2920	.1108	.0116	.0992	8.6	37.95	3.97	33.98	0.64	0.07	0.57
130	0.0708	.0288	.0030	.0258	8.6	40.68	4.24	36.44	2.73	0.27	2.46
150	0.1156	.0478	.0050	.0428	8.5	41.35	4.32	37.03	0.67	0.08	0.59
170	0.1478	.0638	.0072	.0566	8.0	43.17	4.86	38.31	1.82	0.54	1.28
190	0.2496	.1106	.0128	.0978	7.6	44.32	5.12	39.20	1.15	0.26	0.89
210	0.3641	.1670	.0196	.1474	7.5	45.86	5.40	40.46	1.54	0.28	1.26
225	0.6541	.3035	.0384	.2651	6.9	46.40	5.90	40.50	0.54	0.50	0.04

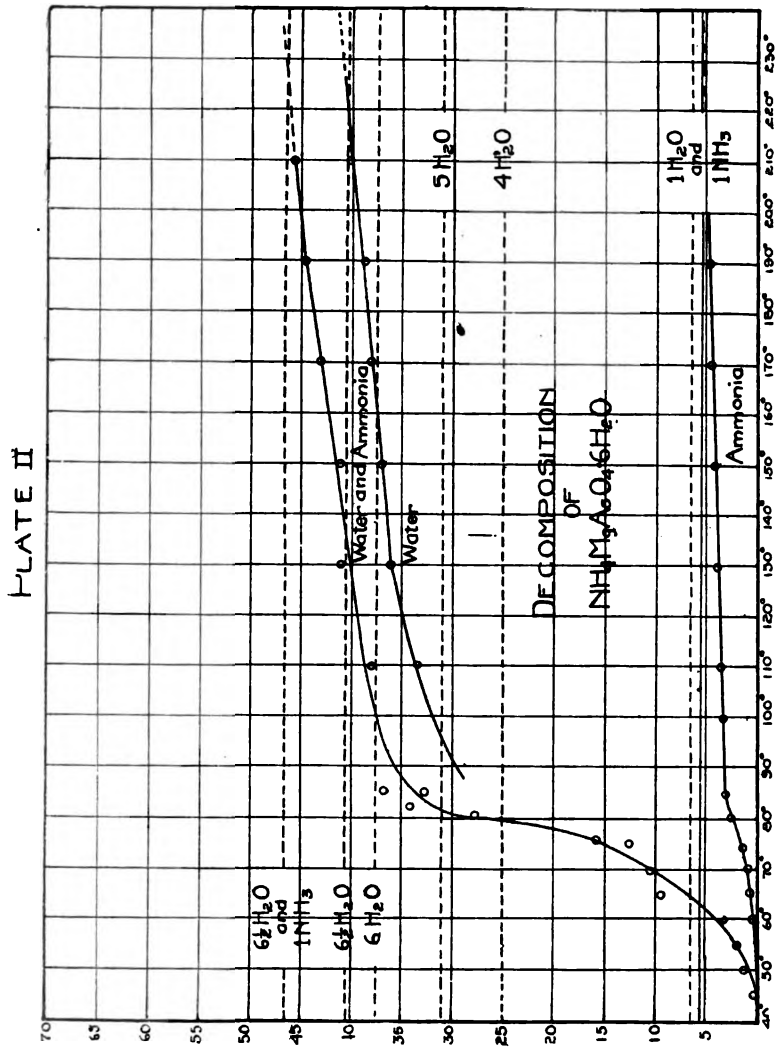
When $NH_4MgAsO_4.6H_2O$ is heated it may sustain any of the following losses or their intermediate per cents.:

Loss of Molecules of	Per cent. of loss
NH_3	5.88
H_2O	6.23
$2H_2O$	12.46
$3H_2O$	18.69
$4H_2O$	24.92
$5H_2O$	31.15
$6H_2O$	37.37
$6\frac{1}{2}H_2O$	40.49
$6\frac{1}{2}H_2O + NH_3$	46.37

The above experimental data plotted with per cents. as ordinates and degrees of temperature as abscissas, give from columns VIII, IX and VII respectively, the curves of evolution of ammonia, water, and both ammonia and water.

[1] These fractional per cents. are obtained by subtracting adjacent total per cents.; they indicate the effect of the *increment* of temperature.

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It will be observed that:

1. Both water and ammonia begin to be given off at 40° and are completely removed at 225°.

2. Fully one-half of all the ammonia is expelled below 80°, the remainder, between temperatures 85-225°.

3. About the *same ratios*[1] of water and ammonia are given off at temperatures 60-210°[2].

[1] Between 60-150° the ratio of weight of water to ammonia averages 8.5 :1, which is equal to a molecular ratio of 8.0 :1. The mass ratio of water to ammonia in NH_4MgAsO_4 is 6.9 : 1. In determining the data for the above table, wide variations from the ratio of 8.5 :1 always indicated experimental errors.

[2] See column VI above. This approximate constancy of ratio is not in evidence with other salts (see $NH_4MgPO_4.6H_2O$) except at high temperatures.

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4. Water is gradually given off below 65°.

5. Then below 80° the remainder of *four* molecules of water is given off[1].

6. The *next two* molecules are given off at temperatures between 80-150°.

7. The *last one-half molecule* of water, derived from the ammonium-oxygen group (NH_4O-), is slowly expelled at temperatures 150-225°; at the last of these temperatures, magnesium pyroarsenate is formed.

The fact that two molecules of water are given off, finally and independently of each other, and of the other four molecules is confirmed by the following experiment. The salt containing the six molecules of water was heated for three hours on the water-bath in closed vessels with a large quantity of ordinary alcohol. After cooling, washing by decantation, first with alcohol, then with ether, and finally drying for a short time in a vacuum dessicator, it was found that dehydration and removal of ammonia from the salt had resulted.

This is shown in the following analyses:

	Per cent. loss
0.3541 grams substances gave 0.2035 grams $Mg_2As_2O_7$ =	25.59
0.4111 grams substances gave 0.3058 grams $Mg_2As_2O_7$ =	25.63
Average	25.61
	Per cent. NH_3
0.0738 grams substances gave 0.0021 grams NH_3	2.85
0.0524 grams substances gave 0.0015 grams NH_3	2.92
Average	2.88

Now the total loss by ignition less the ammonia is equal to the water, 25.61−2.88 = 22.74 per cent. H_2O. Theory $2HMgAsO_4.2H_2O$ = 22.50 per cent. H_2O. Therefore, after dehydrating $NH_4MgAsO_4.6H_2O$ by means of ordinary alcohol, two molecules of water remain, so they must be different from the other four molecules.

This difference of the last two molecules of water from the other four molecules evidently must involve a difference in structure, that is, there must exist for these water molecules different forms of union in the parent molecule. If it is tenable that such *differences of coherence of molecules of water involves differences of structure,* then conversely it may be held that *molecules simultaneously expelled involve similarity of structures.* Now since it is true, as was shown above, that $NH_4MgAsO_4.6H_2O$ possesses two molecules of water differing from one another and from the

[1] It may appear from the curve of evolution of water that *five* and not *four* molecules of water are expelled simultaneously; but it must be remembered that each of the six molecules of water contributes at all lower temperatures its quota, consequently at the decomposition point for four molecules, a surplus derived from the other two and a half molecules will be obtained. The alcohol-dehydrating method establishes beyond a doubt the dissimilarity of four molecules of water, (water of crystallization) from the remainder of water (water of composition).

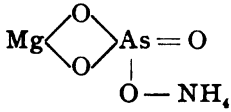
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other four—it is interesting to see what structures will account for all of the facts.

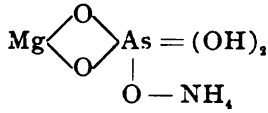
In the first place there can be little doubt that water of crystallization is held in definite molecular structures, and that the structural formula of arsenic acid is :

$$(HO)_3 \equiv As = O$$

and that its ammonium magnesium salt is :



and its salt containing one molecule of water (water of composition) is :



This last structure accounts for the fact that one molecule of water is given off finally and with more difficulty than the other five molecules of water. The fact that the last two molecules of water differ from the other four molecules and differ from each other may be accounted for by the following structure :

$$H - O - Mg - O - As \equiv (OH)_3$$
$$\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad O - NH_4$$

from which on heating one molecule of water would certainly be more easily expelled than the other.[1]

Now since there are four hydroxyls in this structure, they can offer similar points of attachment for four molecules of water (of crystallization), as may be seen individually in the structure :

$$H - \underset{\cdot\cdot}{O} - H$$
$$\qquad\quad \vdots$$
$$\qquad - \underset{\cdot\cdot}{O} - H$$

and completely in the structure :

$$H - \underset{\cdot\cdot}{\overset{\cdot\cdot}{HOH}} - Mg - O - As \equiv (- \underset{\cdot\cdot}{\overset{\cdot\cdot}{HOH}})_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\quad ONH_4$$

[1] Though no data of the relative stabilities of H_3AsO_4 and $Mg(OH)_2$ toward heat are available, it may be inferred, since the former shows greater tendency than the latter to add water, that the hydroxyl attached to magnesium is more easily expelled than the hydroxyl attached to arsenic. However, this point is not so important, here, as the establishment of the structure H — O — Mg — O — As. It seems reasonable to hold that the above condition of magnesium is more probable than as shown in  At any rate the above structure affords the necessary number of points of attachment for all of the water of crystallization and accounts for the constitution of hydrated ammonium magnesium arsenate and other salts.

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This molecular aggregate could split off four molecules of water at or near the same temperature; at a higher temperature, one other molecule of water; and finally and with difficulty the last molecule (and a half) of water.

It may be held that the molecule of water attached to the oxygen in H—O—Mg differs from the three attached to the oxygen in —As—O—H and consequently could involve a difference in coherence in the parent molecule. That *this molecule actually differs* is shown by the data given on page 1161.

It is observed (see plate VI) that one molecule of water is dissociated below 35°, hence all of the facts are in harmony with the above structure.

It may be contented that ammonia does not cohere in the manner indicated by the structure — O — NH_4 but rather in the manner shown in the structure — O — H. Either mode of union is in harmony with

$\dot{N}H_3$

the main structure of ammonium magnesium arsenate as shown above, but the latter of these two perhaps more readily accounts for the ease with which ammonia is expelled at moderate temperatures simultaneously with the water of crystallization. However, it does not explain the fact that the last portions of ammonia are expelled with difficulty and long after all of the "water of crystallization" has retired; nor does it explain the fact that different salts containing the same mass of crystal water manifest varied degrees of coherence for ammonia. These conditions can be explained only on the basis of *composition* of the remainder of the compound, that is, the constituent atoms of the different compounds possess, either individually or collectively, varied affinities for the ammonia group, and for some of the water molecules (water of composition). This is clearly shown in the following studies, wherein (1) the magnesium atom of $NH_4MgAsO_4.6H_2O$ is substituted by calcium and other metals and (2) the arsenic atom is substituted by phosphorus.

Ammonium Calcium Arsenate.

The next salt studied was $NH_4CaAsO_4.6H_2O$, which was prepared as follows according to the suggestion of Wach. Triammonium arsenate (1 part) and ammonium chloride (1 part) were dissolved in a little water and the resulting solution was treated slowly with lime water as long as a precipitate formed. The precipitate consisted of glistening white crystals; after filtering, washing with alcohol, then with ether, and finally drying on filter paper, they were obtained free from traces of chlorine. Analysis of the salt gave the following data :

0.3245 grams substance yielded 0.0827 grams CaO = 18.20 per cent. Ca.
0.7757 grams substance yielded 0.0471 grams NH_3 = 5.61 per cent. NH_4.
0.1464 grams substance lost 0.0636 grams at 190°=43.45 per cent. NH_3+H_2O
0.8244 grams substance lost 0.3616 grams at 200°=43.75 per cent. NH_3+H_2O

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	Theory	Found	Wach [1]	Bloxam [2]
AsO_4	37.70		35.83	34.92
Ca	18.36	18.20	17.52	17.29
NH_4	5.90	5.61	5.37	5.28
$6H_2O$	38.04		41.15	
$NH_3 + 6\frac{1}{2}H_2O$	43.93	43.75		

Evidently the crystals were a purer form of $NH_4CaAsO_4.6H_2O$ than prepared by Wach or by Bloxam. They weathered rapidly; when exposed to air (25°–35°) for four hours they lost 2–20 per cent. in weight.

In the following table the time of decomposition in each case was four hours:

I Temperature	II Weight salt	III Loss of weight H_2O+NH_3	IV NH_3	V H_2O	VI Ratio of both	VII Total H_2O+NH_3	VIII per cent. NH_3	IX loss of H_2O
28	0.2093	.0050			...	2.40	...	
40	0.1854	.0202	.0006	.0196	32.7	10.90	0.33	10.57
41	0.1482	.0202	.0017	.0185	11.0	13.63	1.12	12.51
44	0.1722	.0396	.0032	.0364	11.4	23.00	1.91	21.09
45	0.1642	.0602	.0055	.0547	10.0	36.66	3.32	33.34
59	0.1920	.0690	.0057	.0633	11.1	35.94	2.97	32.97
59	0.1546	.0562	.0044	.0518	11.8	36.35	2.84	33.51
70	0.1240	.0446	.0035	.0411	11.7	35.97	2.82	33.15
80	0.1798	.0686	.0054	.0652	12.1	38.15	3.00	35.15
90	0.1406	.0564	.0047	.0517	11.0	40.11	3.34	36.77
100	0.1448	.0590	.0051	.0552	10.8	40.85	3.50	37.30
104	0.1310	.0540	.0044	.0496	11.3	41.22	3.37	37.85
110	0.1074	.0440	.0040	.0400	10.0	40.97	3.72	37.25
130	0.1516	.0632	.0059	.0573	9.5	41.79	3.90	37.89
150	0.1448	.0620	.0056	.0564	10.0	42.82	3.86	38.96
170	0.1713	.0740	.0067	.0673	10.0	43.20	3.94	39.26
190	0.1394	.0612	.0060	.0552	8.0	43.90	4.29	39.61
200	0.8244	.3616			...	43.75	...	
Red heat	0.4172	.2048			...	49.09	...	
" "	0.3154	.1536			...	48.70	...	

When $NH_4CaAsO_4.6H_2O$ is heated it may sustain any of the following losses or their intermediate per cents.

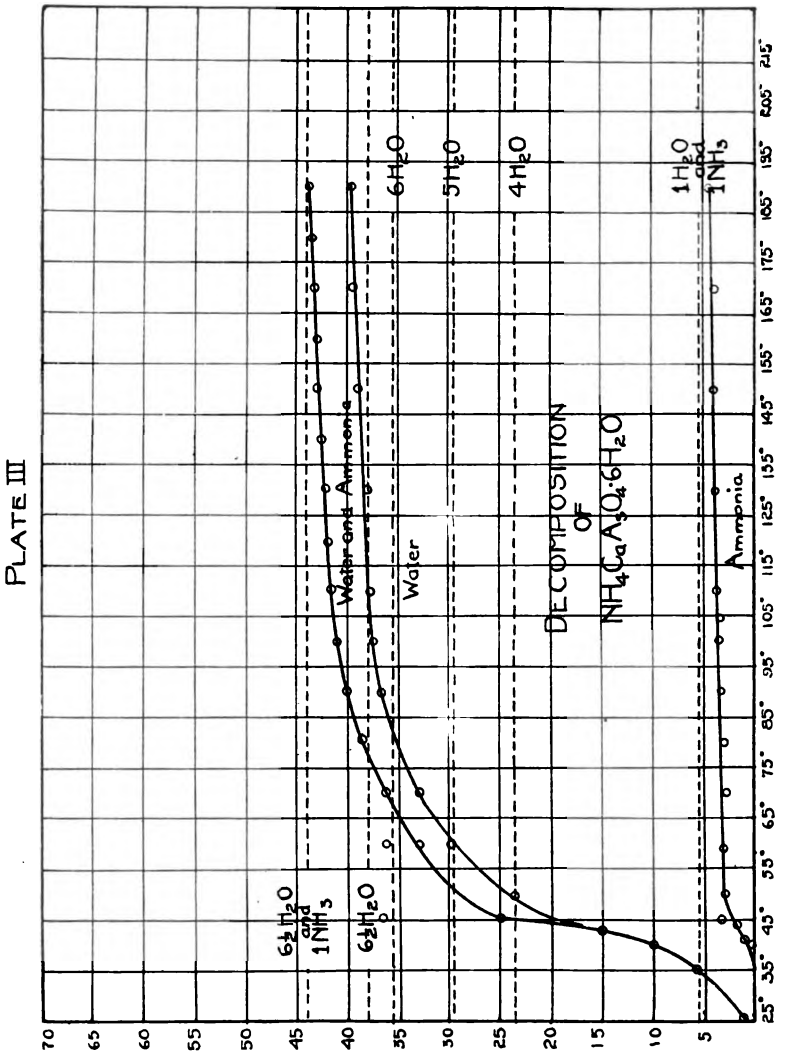
Losses of Molecules of	Per cents. of loss
NH_3	5.57
H_2O	5.90
$2H_2O$	11.80
$3H_2O$	17.70
$4H_2O$	23.60
$5H_2O$	29.50
$6H_2O$	35.40
$6\frac{1}{2}H_2O$	38.36
$6\frac{1}{2}H_2O+NH_3$	43.93

The above data plotted in the manner of Table I gives the following curves.

[1] Schweigger's J. chim. phys., 59, 288.

[2] Chem. News, 54, 168.

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The same misinterpretation of data mentioned in connection with ammonium magnesium arsenate is observed with the calcium salt. Bloxam[1] says on standing 36 days in the air it loses all but one molecule of water; Lefevre[2] says drying at 100° removes all but one-half a molecule of water; Field[3] says it becomes anhydrous at 140°; Kotschubey[4] says it retains one molecule at 125°; and Bloxam[5] assigns formulas (AsO_4)-

[1] Chem. News (1886) **54**, 168.
[2] Ann. chim. phys. [6] **27**, 13.
[3] Jahrsb. 1858, 175.
[4] J. pr. Chem., **49**, 188.
[5] Chem. News (1886) **54**, 169.

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$Ca_3NH_4H_2.3H_2O$ and $(AsO_4)_6Ca_6NH_4H_5.3H_2O$ to the products of drying *in vacuo* over sulphuric acid and drying at 100° respectively. Failure to recognize the fact that the salt begins to decompose at ordinary temperature, and loses both ammonia and water at higher temperatures accounts for these inconsistencies.

It will be observed that:

1. Both water and ammonia are given off more easily from the calcium salt than from the corresponding magnesium salt.

2. The point of greatest decomposition is 40°–50° with the calcium salt instead of 70°–80° as with the magnesium salt.

3. The temperatures at which all ammonia and water are removed is 225° with both salts.

4. The calcium salt like the magnesium salt first liberates one molecule of water then simultaneously three molecules, then one molecule; then another; and finally, the one-half molecule derived from the ammonium-oxy group.

Confirmation of the fact that the last two molecules of water differ from the other four, is secured here as with the magnesium salt by studying the alcohol-dehydration products. The calcium salt was treated twice with alcohol in the same manner as with the magnesium salt; it then gave the following analytical data:

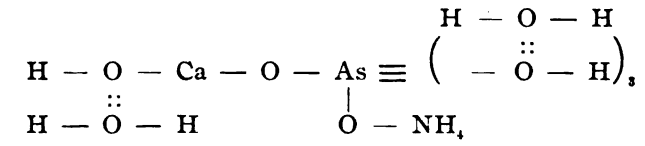
0.5274 grams substance yielded 0.3600 grams $Mg_2As_2O_7$

0.5279 grams substance yielded 0.3670 grams $Mg_2As_2O_7$

0.3274 grams substance yielded 0.0105 grams NH_3

	Theory		Found	
	$HCaAsO_4.2H_2O$	$NH_4CaAsO_4.2H_2O$	I	II
As	34.72	32.18	33.64	33.03
NH_3	0.00	7.32	3.20	

Evidently the salt lost part of its ammonia and contained just two molecules of water. All of the evidence, therefore, seems to favor a structural formula that is perfectly analogous to that of $NH_4MgAsO_4.6H_2O$, viz:—



Other Alkali Earth Salts.

By treating solutions of triammonium arsenate (1 part) and ammonium chloride (1 part) with solutions of strontium hydroxide and barium hydroxide respectively, in exactly the same manner as with calcium hydroxide, it might be expected that the analogous compounds $NH_4SrAsO_4.6H_2O$ and $NH_4BaAsO_4.6H_2O$ would be formed; the precipitates resulting were found, however, to contain no ammonia and only one

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molecule of water. An explanation of this is conceivable when it is recalled that the temperatures of maximum decomposition for the magnesium salt is 70°-80°; for the calcium salt, 40°-50°; and undoubtedly for the strontium and barium salts, below the temperature of formation (room temperature 25°-30°).

The strontium salt prepared in the manner stated was light and fleecy while in suspension and powdery when dry. By dissolving it in hydrochloric acid, adding ammonia to incipient precipitation, filtering and letting stand, the solution yielded beautiful, small, transparent crystals.

I 1.0350 grams powder heated at 350° lost 0.1170 grams

II 0.8820 grams crystals heated at 225° lost 0.0965 grams

	Theory $HSrAsO_4.H_2O$	Found I	Found II
1½ H_2O	11.00	11.29	10.94

The barium salt prepared as above yielded small, pearly crystals,

0.6660 grams substance yielded 0.5257 grams $BaSO_4$

0.4365 grams substance heated at 225° lost 0.0375 grams H_2O

	Theory $HBaAsO_4.H_2O$	Found
Ba	46.44	46.41
1½ H_2O	8.59	8.60

The strontium salt of the above composition had not been prepared hitherto, but undoubtedly its more or less dehydrated form was described by Salkowski[1], Joly[2], Hörman[3], Lefevre[4] and Schiefer[5]. The barium salt is described: Berzelius and Mitscherlich held that it contains one-half molecule of water, the others[6] agree that it contains one molecule of water.

These salts were heated in open crucibles in air baths and yielded the following comparative data:

Temperature	Hours	$HSrAsO_4.H_2O$ Weight	Loss	Loss per cent.	Per cent. of total H_2O
45°	4	0.1152	.0026	2.25	20.45
75°	1½	1.3024	.0621	6.02	54.72
125°	1	1.4923	.1085	7.27	66.10
150°	1	1.5335	.1151	7.56	68.72
210°	1½	0.8612	.0882	10.24	93.09
225°	1	0.8496	.0938	11.04	100.40
350°	1	1.0350	.1170	11.29	109.63
Red Heat	⅕	1.0350	.1470	14.28	129.82

[1] J. pr. Chem., **1868**, 148.

[2] Compt. rend., **104**, 905.

[3] Inaug. Diss., 1879.

[4] Ann. chim. phys., (6) **27**, 20.

[5] Zeitschrift für die gesammten Naturwissenschaften **23**, 364.

[6] J. pr. Chem., **49**, 189; Ibid., **104**, 139; Ibid., **40**, 247. Compt. rend., **58**, 253; Lehrbuch der Chemie von Berzelius; Lehrbuch der Chemie von Mitscherlich.

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Per cent. of total H_2O	Loss per cent.	$HBaAsO_4.H_2O$ Loss	Weight	Hours	Temperature
0.85	0.07	.0008	1.0914	1	60°
3.61	0.31	.0050	1.6078	1	115
29.57	2.54	.0311	1.2347	1	135
71.59	6.15	.0804	1.3067	1	150
71.36	6.13	.0986	1.6078	1	190
95.34	8.19	.0966	1.1790	1⅓	210
99.88	8.58	.0643	0.7496	1	225
123.05[1]	10.57	.1246	1.1790	1/5	Red Heat

When these salts are heated they suffer the following or intermediate losses:

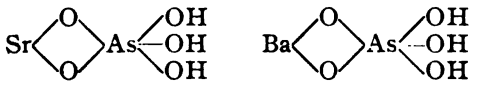
	$HSrAsO_4.H_2O$	$HBaAsO_4.H_2O$
H_2O	7.33	5.73
$1\frac{1}{2}H_2O$	11.00	8.59

and yield the corresponding pyroarsenates. It will be observed in the above table that:

1. The strontium salt gradually loses its molecule of water below 125°; the barium salt loses its molecule of water below 150°.

2. Both salts, like the magnesium and calcium salts studied, lose all water at 225°.

The fact that the arsenic atom has no affinity above 225° for the last hydroxyl in these four salts studied shows that there must exist in them the same structure: As≡O—H. Furthermore since these four salts exhibit little difference in the ease of dissociating the last molecule of water, differences that can be attributed to variation of size of salt crystals used, etc., it is tenable that the last molecule of water is held as shown in the structure: $=As—(OH)_3$, consequently the above-mentioned strontium and barium salts must possess the following structural formulas:



Furthermore it may be gathered from the above experiments that when hydrated ammonium salts, or hydrated salts containing no ammon-

[1] When ammonium calcium arsenate and these two salts are heated in crucibles to temperatures higher than 225°, say by igniting to a red heat, there results to some extent the following reactions: $3M_2As_2O_7 = 2M_3(AsO_4)_2 + As_2O_5$, $As_2O_5 = As_2O_3 + O_2$. Evidences for these reactions are as follows: first, the residue, easily soluble in hydrochloric acid, shows the presence of arsenate, but no arsenite; secondly, a sublimate obtained on heating in tubes, yields tests for both oxides. This loss with the calcium salt was mentioned by Wach[2] and Lefevre[3]; the second reaction is described by Kopp[4], the stability of $Ca_3(AsO_4)_2$ toward heat is confirmed by Simon[5].

[2] Schwiegger's J. Chem. Physik., 59, 265.

[3] Ann. chim. phys., (6) 27, 56.

[4] Ibid, (3) 48, 106; Jahrsb., 1856, 385.

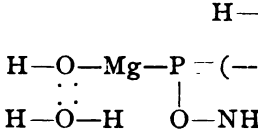
[5] Ann. Physik. ü Chem., Pogg., 40, 417.

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ia begin to decompose, *fractions from each molecule of water (and of the ammonia) are given off at all temperatures lower than the ones at which individually they are completely dissociated;* therefore, for instance in $NH_4MgAsO_4.6H_2O$, from which 1 mol. NH_3, 1 mol. H_2O, 3 mols. H_2O, 1 mol. H_2O, and 1 mol. H_2O are separately dissociated, *all of the higher dissociations are taking place fractionally and simultaneously when any of the lower dissociations are taking place partially or completely*, hence within the range of temperatures of dissociation, *no definite formula can be assigned to the residues.*

Salts of Phosphoric Acid.

It was shown above that substitution of alkali earths elements in $NH_4MgAsO_4.6H_2O$ produced complexes more easily decomposed than the magnesium salt; it now remains to show the effect of substitution of phosphorus for arsenic in $NH_4MgAsO_4.6H_2O$. It was found as a matter of fact that this salt, though more stable than the arsenic salts, decomposes in the same manner and consequently must possess a similar structural formula:



The samples of $NH_4MgPO_4.6H_2O$ used were found by ignition to be absolutely pure; and in the following experiments were heated for four hours, except fractions indicated by temperatures 148-205°, which were heated for 7 hours each (table IV).

When heated, $NH_4MgPO_4.6H_2O$ may sustain any of the following molecular loses or their intermediate per cents:

Loss of Molecules of	Per cent. of loss
NH_3	6.93
H_2O	7.34
$2H_2O$	14.70
$3H_2O$	22.04
$4H_2O$	29.39
$5H_2O$	36.74
$6H_2O$	44.08
$6\frac{1}{2}H_2O$	47.34
$6\frac{1}{2}H_2O + NH_3$	54.70

It is seen on comparing Plates II and IV that:

1. Both ammonium magnesium arsenate and ammonium magnesium phosphate sustain maximum decompositions between 70° and 80°.

2. The former begins to decompose below 40°; the latter at 45°.

3. The former is completely decomposed at 225°; the latter is not completely decomposed at 360°.

4. Half of the ammonia of the former is liberated below 80°; half of the ammonia of the latter is liberated below 155°.

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TABLE IV

I Temperature	II Weight of Salt	III Loss of weight of H_2O+NH_3	IV Loss of weight of NH_3	V Loss of weight of H_2O	VI Ratio of Both	VII Total per cent. loss H_2O+NH_3	VIII per cent. loss NH_3	IX per cent. loss H_2O
40	.5810	.0000	.0000	.0000	0.0	0.00	0.00	0.00
45	.9808	.0060	.0005	.0055	11.0	0.61	0.05	0.56
50	.4926	.0120	.0009	.0111	12.3	2.44	0.18	2.26
55	.3129	.0108	.0006	.0102	17.0	3.26	0.19	3.07
60	.5400	.0193	.0016	.0177	11.1	3.57	0.30	3.27
65	.4921	.0247	.0020	.0227	11.3	5.02	0.41	4.61
70	.7473	.0423	.0042	.0381	9.1	5.66	0.56	5.10
76	.5140	.1763	.0030	.1463	48.8	34.30	0.59	33.71
80	.6504	.2341	.0040	.2301	57.5	36.00	0.61	35.39
95	.2254	.0822	.0016	.0806	50.4	36.47	0.71	35.76
110	.4260	.1557	.0032	.1525	47.9	36.55	0.75	35.80
127	.1674	.0624	.0013	.0611	47.0	37.28	0.77	36.51
135	.1249	.0487	.0010	.0477	47.7	39.06	0.80	38.26
148	.1620	.0664	.0021	.0643	30.5	40.98	1.30	40.68
155	.1126	.0514	.0040	.0474	11.8	45.65	3.55	42.10
165	.0926	.0436	.0041	.0395	9.6	47.08	4.42	42.66
175	.0900	.0436	.0043	.0393	9.1	48.45	4.77	43.68
186	.0680	.0336	.0033	.0303	9.2	49.41	4.85	44.56
195	.0526	.0260	.0026	.0234	9.0	49.50	4.94	44.56
200	.1251	.0624	.0065	.0559	8.6	49.88	5.19	44.69
205	.1387	.0702	.0073	.0629	8.6	50.61	5.26	45.35
225	.4734	.2342			..	50.53		
230	.9374	.4726			..	50.52		
240	.9374	.4818			..	51.39		
295	.9374	.4950			..	52.50		
310	.6631	.3494			..	52.70		
340	.6631	.3514			..	53.00		
360	.3194	.1704			..	53.33		
Red heat.	.8724	.4767			..	54.63		

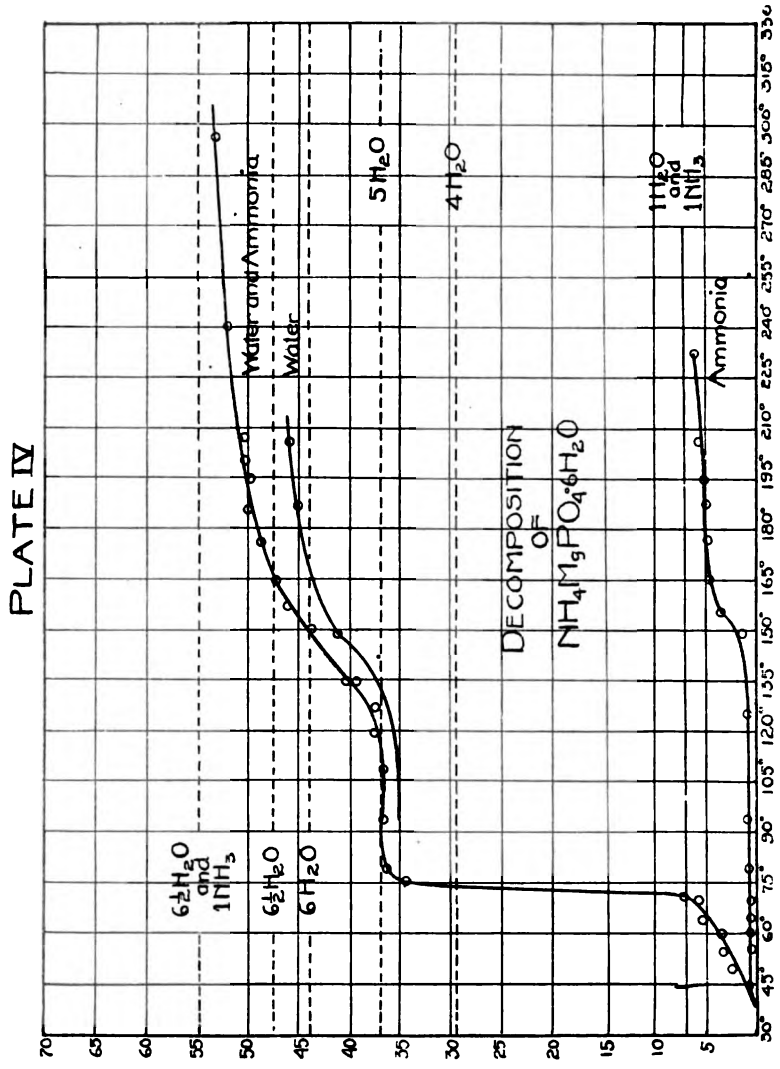
5. With both salts, first one molecule of water is liberated; then simultaneously, three molecules; then one molecule; again one molecule; and finally the last one-half molecule[1].

When $NH_4MgPO_4.6H_2O$ was heated with alcohol in the manner that the corresponding arsenic salt was, similar dehydration and removal of ammonia were incurred. After a sample was heated for three hours, it gave the following analytical data:

0.4522 grams lost by ignition 0.1460 grams = 32.29 per cent.
0.4057 grams lost by ignition 0.1230 grams = 32.04 per cent.
Average = 32.16 per cent.
0.1651 grams yielded 0.0026 gram NH_3 = 1.59 per cent.
Therefore H_2O = 32.16 — 1.59 = 30.57 per cent.

[1] Here as with the corresponding arsenic salt, *five* molecules of water are apparently given off simultaneously; the explanation here is the same as there.—The curve here shows a liberation of *one* molecule of water below 67°. This harmonizes with the above formula wherein the molecule of water attached to H—O—Mg—O— differs from the other three molecules of "water of crystallization."

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Another sample was heated for two hours with alcohol and the treatment with alcohol was repeated; the salt then gave the following analytical data:

0.4539 grams lost by ignition 0.3189 grams = 29.74 per cent.
0.4002 grams lost by ignition 0.2811 grams = 29.79 per cent.
Average = 29.76 per cent.
0.0676 grams yielded 0.0006 grams NH_3 = 0.89 per cent.
0.1201 grams yielded 0.0011 grams NH_3 = 0.95 per cent.
Average = 0.92 per cent.
Therefore H_2O = 29.76 − 0.92 = 28.84 per cent.
Theory of H_2O in $HMgPO_4.2H_2O$ = 28.84 per cent.

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Therefore, upon heating ammonium magnesium phosphate with alcohol the following reaction takes place:

$$NH_4MgPO_4.6H_2O = HMgPO_4.2H_2O + 4H_2O + NH_3$$

Microcosmic Salt.

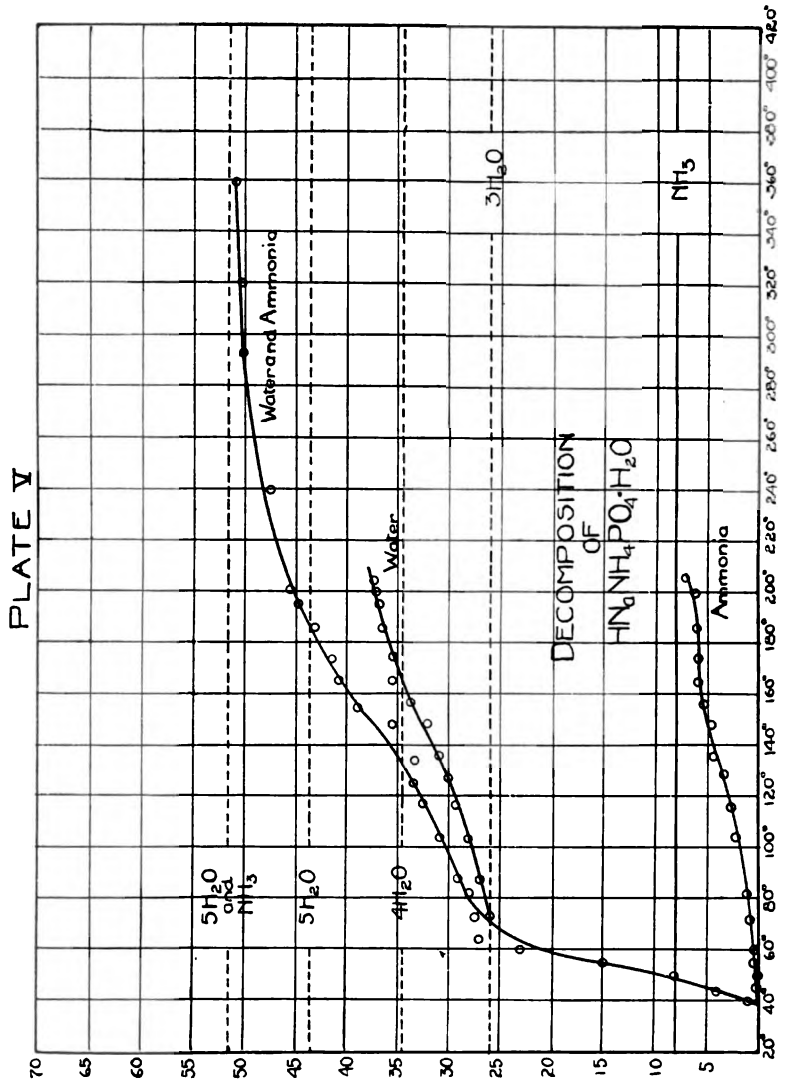
This salt yielded comparative data with greater difficulty than any other salt studied. The cause of this was ultimately found to be owing to variations in size of crystals used. After pulverizing and passing them through the sieve, little difficulty was encountered.

I	II	III	IV	V	VI	VII	VIII	IX	X
Temper-		Weight	Loss of weight of			Ratio	Total	per cent.	loss of
ature	Time	of Salt	H_2O+NH_3	NH_3	H_2O	of Both	H_2O+NH_3	NH_3	H_2O
40	4	2.1818	.0254	.0008	.0246	30.7	1.16	0.04	1.12
45	4	1.3590	.0498	.0009	.0489	54.4	3.66	0.07	3.59
50	4	0.9220	.0788	.0009	.0779	86.5	8.55	0.10	8.45
55	4	0.3876	.0683	.0013	.0670	51.5	17.62	0.36	17.26
60	4	0.4848	.1138	.0020	.1118	55.9	23.26	0.43	22.93
64	3	0.4520	.1226	.0032	.1194	37.3	27.13	0.71	26.42
72	4	0.1205	.0332	.0011	.0321	29.2	27.61	0.89	26.72
83	3	0.4439	.1262	.0054	.1208	22.3	28.44	1.23	27.21
88	4	0.8261	.2404	.0124	.2280	18.4	29.10	1.50	27.60
104	4	0.4764	.1477	.0105	.1372	13.0	31.00	2.20	28.80
116	4	0.2786	.0801	.0078	.0723	9.3	32.75	2.80	29.45
127	4	0.1898	.0630	.0063	.0567	9.0	33.29	3.32	29.97
135	4	0.1656	.0586	.0071	.0515	7.2	35.39	4.29	31.10
148	4	0.2310	.0840	.0105	.0735	7.0	36.46	4.54	31.92
155	4	0.1219	.0477	.0064	.0413	6.4	39.13	5.49	33.64
165	4	0.1664	.0680	.0095	.0585	6.1	40.86	5.70	35.16
175	4	0.1026	.0422	.0058	.0364	6.3	41.13	5.65	35.48
186	4	0.0680	.0289	.0039	.0250	6.4	42.50	5.74	36.76
195	4	0.0818	.0364	.0050	.0314	6.3	44.50	6.11	38.39
200	4	0.1016	.0459	.0063	.0396	6.3	45.18	6.20	38.98
205	4	0.1648	.0758	.0122	.0636	5.2	46.00	7.40	38.60
240	2	0.6130	.2235			..	46.95		
295	2	1.2261	.6154			..	50.19		
310	4	1.0204	.5152			..	50.49		
360	3	0.5070	.2558			..	50.40		
Red heat	1/5	0.9328	.4760			..	51.02		

When microcosmic salt decomposes it may sustain any of the following or intermediate losses:

NH_3	8.13
H_2O	8.61
$2H_2O$	17.22
$3H_2O$	25.83
$4H_2O$	34.45
$5H_2O$	43.05
$4H_2O+NH_3$	42.58
$5H_2O+NH_3$	51.20

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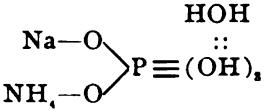


It is observed that:

1. Three molecules of water are expelled simultaneously below 62°.
2. The fourth molecule of water is expelled below 160°.
3. The last molecule of water here as with ammonium magnesium phosphate is not completely removed at 360°.
4. The ammonium molecule is expelled in nearly the same manner as with ammonium magnesium phosphate.

All of the facts seem to support the following structural formula for microcosmic salt:

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which upon being heated liberates first the three molecules of water held by tetravalent oxygen; then the molecule derived from two hydroxy groups; and finally the molecule of water derived from the ammonium-oxy and the remaining hydroxyl group.

Further evidence that microcosmic salt contains three molecules of water that are similar in the ease of dissociating, and consequently that they possess similar structural attachments, is derived by the alcohol-dehydration method. After heating twice with alcohol for one hour, the residue contained 9.60 per cent. ammonia and yielded, by ignition, a loss of 45.70 per cent., or a loss of only a fraction of one molecule of water had been sustained.

Vapor Pressure Determinations.

When the vapor pressures of ammonium magnesium arsenate are carefully determined a distinct break in its curve (vide Plate VI) is noticeable below 35°, indicating the liberation of one molecule of water at this temperature. The following data represent two different determinations:

SERIES I

Temperature	Pressure	Temperature	Pressure	Temperature	Pressure
27	0.61	37	6.96	45	11.70
28	0.92	38	7.62	46	13.08
29	1.23	39	7.65	47	13.80
32	2.48	40	7.67	48	14.50
34	4.36	41	9.01	49	15.90
35	5.65	43	9.70	50	17.30
36	6.30	44	10.40	51	19.40

SERIES II

Temperature	Pressure	Temperature	Pressure	Temperature	Pressure
31.5	3.00	35.5	7.50	44	10.6
32.0	4.25	40.5	8.00	49	14.5
33.0	5.50	42.0	9.30	54	18.0

When this salt is heated at once to temperatures of 70°–98°, other conditions remaining the same, the phenomenon of "suspended transformation" becomes manifest, as is shown in Plate VI and the following data:

SUSPENDED TRANSFORMATION

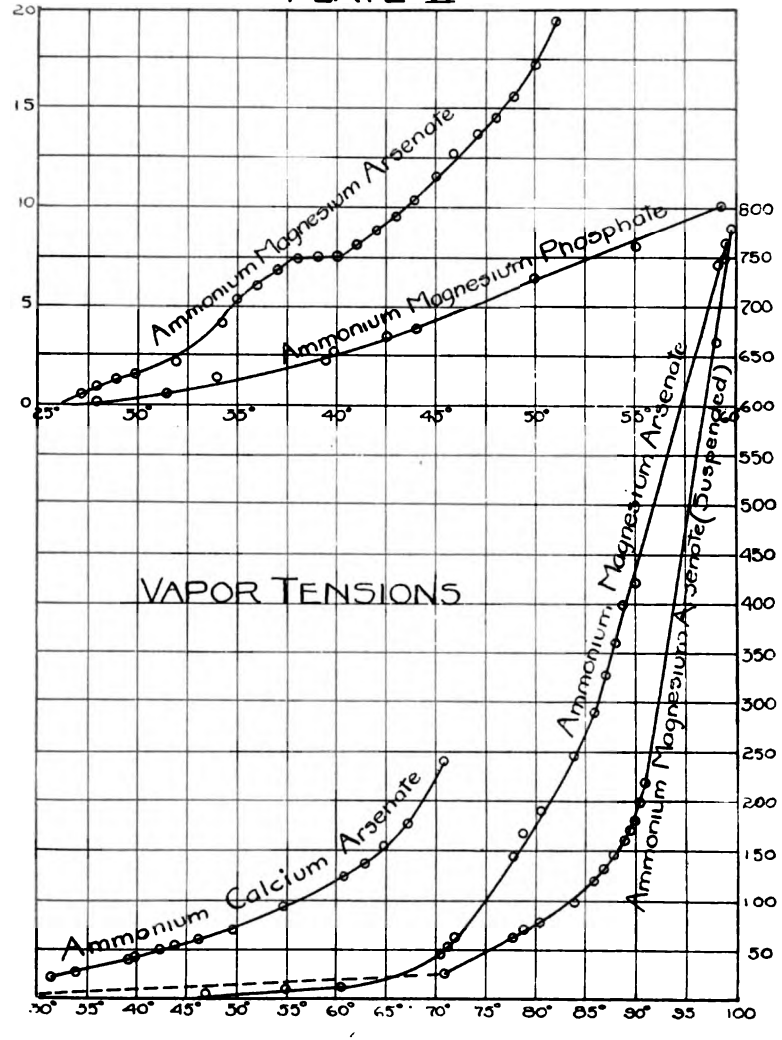
Temperature	Pressure	Temperature	Pressure	Temperature	Pressure
30.0	10.70	86.	120.5	90.	186
71.2	29.02	86.9	136.8	90.5	204
78.0	65.26	88.	150.	91.	225
79.0	73.92	89.	167.	98.	670
80.3	81.88	89.4	177.	98.7	776
83.8	101.75				

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NON-SUSPENDED TRANSFORMATION

Temperature	Pressure	Temperature	Pressure	Temperature	Pressure
45.5	1.39	72	63.6	88.	364.5
47.0	6.34	78	148.7	89	404.8
50.2	7.11	79	169.0	89.4	417.0
55.2	9.38	80.3	194.0	90	424.0
60.6	14.79	81.4	219.8	91	482.0
64.0	21.78	83.8	247.3	92	559.0
70.5	45.27	86	291.0	98	745.1
71.2	53.54	87	331.5		

PLATE VI



Though the general forms of these two curves are similar, it is observed (1) that the normal pressures are not exerted when the salt is heated *at*

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once to 70° and (2) that this condition of suspended transformation is lost at 99°. Evidently the cause of this condition is the formation of a superficial impervious layer of dehydrated substance that protects the inner portions from immediate decomposition.

The vapor pressures of the other curves are given in the following tables:

AMMONIUM CALCIUM ARSENATE[1].

Temperature	Pressure	Temperature	Pressure	Temperature	Pressure
31.5	25.6	44.0	55.2	62.7	136.9
34.0	29.5	46.5	61.2	65.1	161.6
39.4	40.8	50.0	73.6	67.4	188.3
40.0	45.3	55.0	93.6	70.2	222.7
42.5	50.5	60.8	124.5	70.8	246.3

AMMONIUM MAGNESIUM PHOSPHATE[1].

Temperature	Pressure	Temperature	Pressure	Temperature	Pressure
28.0	10.36	40.0	12.82	50.0	16.54
31.5	10.79	42.5	13.26	55.0	17.92
34.0	11.57	44.0	14.06	58.5	20.02
39.4	12.43	46.5	15.27		

VAPOR PRESSURES[2]

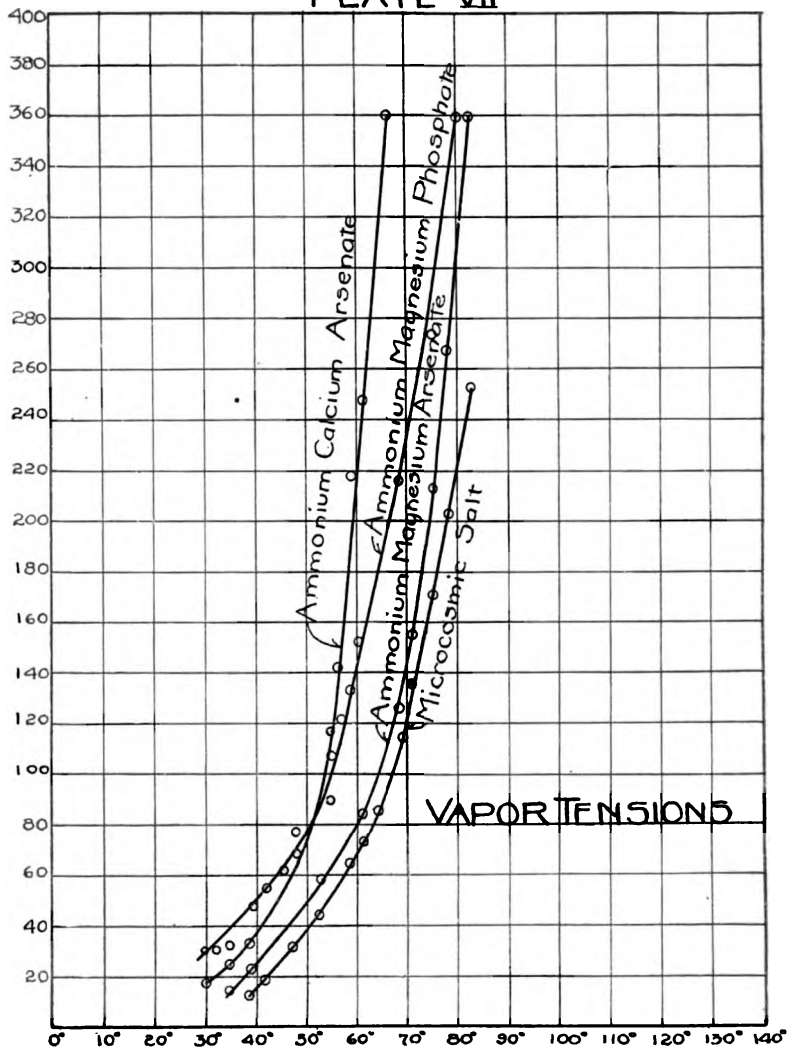
Temperature	$HNaNH_4PO_4.4H_2O$	$NH_4MgAsO_4.6H_2O$	$NH_4MgPO_4.6H_2O$	$NH_4CaAsO_4.6H_2O$
30.6	...	...	30.0	...
32.8	...	...	32.0	19.5
35.0	...	14.5	37.0	25.3
39.0	12.0	23.0	47.0	34.0
42.2	17.0	...	54.3	45.0
45.0	30.0	...	61.5	...
47.8	...	30.3	75.0	65.6
48.0	...	33.0	77.0	69.0
52.5	44.0	58.0	...	...
55.0	45.5	...	89.0	106.0
55.3	...	...	95.5	117.0
56.8	...	...	120.0	141.0
59.0	65.0	70.0	132.5	217.0
61.0	73.0	84.0	151.0	246.5
64.5	85.0	85.0	176.5	390.0
68.7	113.0	125.0	215.0	407.0
70.8	134.0	137.5	239.0	...
71.2	148.3	154.0	240.6	...
75.0	170.0	212.0	273.0	...
78.0	201.0	267.0	330.2	...
82.5	252.5	405.0	418.0	...

[1] All vapor pressures mentioned thus far were determined in Dehn's tensimeter. (This Journal, 29, 1052.) The break in the curve represented by the expulsion one of molecule of water from ammonium magnesium phosphate is not plainly marked; however the vapor pressures here were not determined with the greatest of care.

[2] These vapor pressures were determined in the Bremer-Frowein form of tensimeter (Phys. Chem., 1, 5; 17, 52), and, being only approximately correct, are useful here only in showing relative pressures at higher temperatures.

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PLATE VII



Further studies by the methods herein expressed are being made; at present one may safely draw the following:

Conclusions.

1. Hydrated ammonium salts upon being partially or largely dehydrated yield products of indefinite composition, for the reason that

2. These salts at elevated temperatures undergo primary or secondary decompositions of all of the different dissociating molecules of water and ammonia, consequently

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3. Drying on the water-bath or "drying to constant weight" cannot yield homogeneous products, and therefore,

4. Many of the empirical formulas of such compounds given in the literature are necessarily incorrect.

5. The affinity and manner of union of water of composition do not differ largely from the affinity and manner of union of ammonia.

6. Water of crystallization, conforming to the law of definite proportions, must be held in definite molecular structures, through the agency of valency, as in other compounds.

7. Tetravalent oxygen, necessary to express these structures, is loosened at temperatures above 100°, therefore salts usually expell water of crystallization below this temperature and water of composition above this temperature.

8. Finding dissimilar molecules of water in hydrated salts, leads to a conception of their structure.

URBANA, ILLINOIS.
May 29, 1907.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 15.]

THE SPECIFIC HEAT OF SOLIDS AT CONSTANT VOLUME, AND THE LAW OF DULONG AND PETIT.

BY GILBERT NEWTON LEWIS.

Received Jan. 28, 1907.

The study of the relation between the specific heat of gases at constant volume and at constant pressure has led to a number of important theoretical conclusions, but in the case of solids and liquids we have been familiar hitherto only with the specific heat at constant pressure. To determine experimentally the specific heat at constant volume of a liquid or solid would be a difficult undertaking. Fortunately it is possible, assuming nothing more than the validity of the two laws of thermodynamics, to calculate this important quantity from existing data.

The internal energy at constant temperature is nearly independent of the volume, in the case of a gas, but may vary considerably with the volume in the case of a liquid or solid. Except in rare cases it increases with increasing volume. The difference between the specific heats at constant pressure and constant volume is chiefly due to this change of internal energy with the volume, as I have shown in a previous paper[1] where the following purely thermodynamic equation was obtained.

$$c_p - c_v = \left(\frac{\partial v}{\partial T}\right)_P \left[P + \left(\frac{\partial E}{\partial v}\right)_T\right] \qquad (1)$$

c_p and C_v are the two specific heats. E and v are respectively the in-

[1] Lewis. The Development and Application of a General Equation for Free Energy and Physico-Chemical Equilibrium Equation 38. Pr. Am. Acad., 35, 1 (1899); J. physic. Chem., 32, 364 (1900).

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ternal energy and the volume of one gram of the substance at the absolute temperature T and the pressure P.

Besides this equation we have the fundamental thermodynamic equation connecting the pressure and temperature of any substance, namely,

$$P + \left(\frac{\partial E}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v \qquad (2)$$

Combining these two equations, we have,

$$c_p - c_v = T\left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_v$$

Now by the principles of partial differentials,

$$\left(\frac{\partial P}{\partial T}\right)_v = -\frac{\left(\frac{\partial v}{\partial T}\right)_P}{\left(\frac{\partial v}{\partial P}\right)_T}$$

Hence

$$c_p - c_v = -T\frac{\left(\frac{\partial v}{\partial T}\right)^2_P}{\left(\frac{\partial v}{\partial P}\right)_T} \qquad (3)$$

The coefficient of compressibility α and the coefficient of thermal expansion β as commonly used are defined by the equations,

$$\alpha = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T, \text{ and, } \beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$$

Combining these equations with (3) we have,

$$c_p - c_v = \frac{T\beta^2 v}{\alpha} \qquad (4)$$

This exact thermodynamic equation enables us from the specific heat at constant pressure to calculate the specific heat at constant volume for any substance when its coefficients of compressibility and of thermal expansion are known.

According to the theory of van der Waals the specific heat at constant volume for any unassociated substance should be the same in the liquid and the gaseous states, and this conclusion has been very generally accepted.[1] Equation (4) gives a means of testing this view directly, and I hope soon to discuss this interesting question more at length. In the present paper the above principles will be employed in the calculation of the specific heats at constant volume of the solid elements. The importance of this application of equation (4), in view of the law of Dulong and Petit, was called to my attention by Prof. A. A. Noyes.

If in equation (4) the gram atom is used as unit of mass in place of the gram, c_p and c_v must be replaced by C_p and C_v, the corresponding atomic heats, and v must be replaced by V, the atomic volume. If the unit of pressure chosen is the megadyne per square centimeter, or the

[1] See Nernst, Theoretische Chemie (Edit 4), p. 240.

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megabar, and the unit of volume is the cubic centimeter, then C_p and C_v will have the dimensions of megergs per degree. If we prefer to express these in calories per degree the factor 41.78 must be introduced, and equation (4) becomes:

$$C_p - C_v = \frac{T\beta^2 V}{41.78\,\alpha}$$

The accompanying table contains the results obtained by applying equation (5) to all the solid elements for which α and β are known, with the exception of the non-metals of atomic weight lower than 35. The latter are the elements which deviate radically from the law of Dulong and Petit. The values given are all for 20°, since for this temperature the very careful determinations of compressibility made by T. W. Richards and his collaborators are available. From their work[1] the first three columns of the table are taken directly. The first gives the approximate atomic weight of the elements; the second, the atomic volumes in cc.; the third, the coefficients of compressibility, pressure being measured in megadynes per sq. cm. The fourth column gives the coefficients of thermal expansion. These are taken from the tables of Landolt and Börnstein, interpolated as well as possible for 20°. The fifth column contains the values of $C_p - C_v$, in calories per degree, calculated by equation (5). The sixth column contains the atomic heats at constant pressure, expressed in calories per degree. The values obtained by Gaede[2] for Sb, Pb, Cd, Cu, Pt, Zn, and Sn, in the neighborhood of 20°, are taken directly from his work. The other values are taken from the tables of Landolt and Börnstein, interpolated for 20° by means of the temperature coefficients obtained by Richarz and Wigand.[3] In some cases a certain amount of choice was possible in selecting the most probable value of the specific heat. But this choice was made in every case before the final calculations were made, in order to make sure that the selection was without prejudice. The seventh column (Δ_1) shows the deviations of the several values of C_p from the mean. The eighth column gives the values of the atomic heat at constant volume in calories per degree. The last column (Δ_2) shows the deviations of the several values of C_v from the mean. In the last five columns only one decimal place is given. For a number of elements another place would be without significance, owing to the unreliability of the data for α and C_p.

The table shows that the mean value of C_v for the nineteen elements is three-tenths of a unit below the mean of C_p. The average deviation of the individual values from the mean is considerably less for C_v than for C_p. Probably except in the case of sodium and potassium the values

[1] Publication of the Carnegie Institution, 76 (1907).

[2] Physik. Z. 4, 105 (1902).

[3] Ann. d. Phys. (4) 22, 64 (1907).

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	1 At. wt.	2 V	3 $\alpha \times 10^6$	4 $\beta \times 10^6$	5 $C_p - C_v$	6 C_p	7 Δ_1	8 C_v	9 Δ_2
Na	23.0	23.7	15.4	72.	0.5	6.9	0.7	6.4	0.5
Mg	24.4	13.3	2.7	25.	0.2	6.0	0.2	5.8	0.1
Al	27.1	10.1	1.3	23.	0.2	5.8	0.4	5.7	0.3
K	39.1	45.5	31.5	83.	0.6	7.1	0.9	6.5	0.6
Fe	55.9	7.1	0.40	10.	0.1	6.0	0.2	5.9	0.0
Ni	58.7	6.7	0.27	13.	0.2	6.1	0.1	5.9	0.0
Cu	63.6	7.1	0.54	16.	0.2	5.8	0.4	5.6	0.3
Zn	65.4	9.5	1.5	29.	0.3	6.0	0.2	5.6	0.2
Pd	107.	9.3	0.38	11.	0.2	6.1	0.1	5.9	0.0
Ag	107.9	10.3	0.84	19.	0.3	6.1	0.1	5.8	0.1
Cd	112.5	13.0	1.9	28.	0.3	6.2	0.0	5.9	0.5
Sn	119.	16.2	1.7	22.	0.3	6.4	0.2	6.1	0.2
Sb	120.	17.9	2.2	11.	0.1	6.0	0.2	5.9	0.0
I	127.	25.7	13.	84.	0.9	6.9	0.7	6.0	0.1
Pt	195.	9.1	0.21	9.	0.2	6.1	0.1	5.9	0.0
Au	197.	10.2	0.47	14.	0.3	6.2	0.0	5.9	0.0
Tl	204.	17.2	2.6	28.	0.3	6.4	0.2	6.1	0.2
Pb	207.	18.2	2.2	29.	0.4	6.3	0.1	5.9	0.0
Bi	208.	21.2	2.8	13.	0.1	6.3	0.1	6.2	0.3
Average						6.2 +	0.26	5.9 +	0.15
Average excluding the first four						6.2	0.18	5.9	0.09

of Δ_2 are in no case greater than the possible error in C_v due to experimental errors. If the first four elements are excluded the mean value of C_p for the remaining fifteen is 6.2, and the average deviation from this mean is 0.18. The mean value of C_v is [illegible], and the average deviation is 0.09, only one-half the average deviation from C_p. This result is certainly not accidental. The law of Dulong and Petit may therefore be modified and stated as follows: *Within the limits of experimental error the atomic heat of constant volume, at 20°, is the same for all the solid elements whose atomic weights are greater than that of potassium.*

Whether this law will also be true for other temperatures cannot be ascertained until the change of compressibility with the temperature has been investigated. C_p in many cases increases rapidly with the temperature, but the term $C_p - C_v$ probably increases also. It is not unlikely therefore that C_v may be nearly independent of the temperature.

RESEARCH LABORATORY OF PHYSICAL CHEMISTRY.
Massachusetts Institute of Technology, June 25, 1907.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 140.]

MOLTEN HYDRATED SALTS AS SOLVENTS FOR THE FREEZING POINT METHOD[1].

BY J. LIVINGSTONE R. MORGAN AND H. K. BENSON.

Received June 11, 1907.

The depression of the freezing point of a solvent by the addition to it of a soluble substance has been employed now for a number of years as a

[1] Abstract from the Dissertation (Columbia 1907) of H. K. Benson.

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means of determining the molecular weight, in solution, of the dissolved substance. Liquids of almost all types have been systematically studied as solvents for this purpose, but, with one exception, no results have been obtained for solutions in the liquids formed by the melting of salts containing water of crystallization. Löwenherz[1] using molten $Na_2SO_4.10H_2O$ for this purpose, has found that it may be used just as any other liquid, except that it prevents or drives back the ionization when the substance added has an ion in common with it. The object of this investigation is the similar study of other molten hydrated salts, to ascertain whether or not this behavior is general.

The salts employed melt to form a clear liquid at comparatively low temperatures, and fulfil the condition necessary for the method, *i. e.*, on cooling, even in the presence of a second substance, they separate a solid phase of the same composition as the liquid.

The apparatus employed was the form designed by Smeaton, in which the stirring of both the cooling bath and the solution, after infection, is continuous, the stirrers being driven by a small motor. The temperatures were read either on a normal thermometer (G.S. No. 5853, 1903) reading to 0.02° or on a Beckmann reading to 0.01°. The cooling bath was retained at a temperature from 4–8° below the freezing point of the pure solvent; and the over-cooling was kept within 1° when possible; and when not, the concentrating effect was accounted for by the aid of the formula giving the fraction (f) of solvent separated; *i.e.*, $f = \Delta t \frac{c}{w}$, where c is the specific heat as liquid, w is the latent heat of fusion, (both at the freezing point of the pure solvent) and Δt is the over-cooling in degrees.

In every case the separation of solid was induced by infection with a crystal and it was ascertained by analysis that the solid phase which separated had the same composition as the pure liquid solvent.

Preparation of the Solvents.

$CaCl_2.6H_2O$. The pure hexahydrate of calcium chloride melts in its own water of crystallization at 29°.48. Kahlbaum's pure salt was melted, over-cooled, infected with a crystal, and the solid separated drained from adherent liquid. This process was continued until the freezing point of the molten solid was constant at 29°.48.

To obtain the molecular depression of the freezing point in this solvent use was made of the relation $K = \frac{0.02\,T^2}{w}$ where w is the heat of fusion of 1 gram of solvent, *i.e.*, 40.7[2] calories, and T is its absolute freezing point, 29°.48 + 273°. Substituting these data, we find K = 45.0.

[1] Z. physik. Chem., 18, 70, (1895).

[2] Tammann, Kristallisieren und Schmelzen, p. 45.

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$LiNO_3.3H_2O$. This salt was prepared in the same way as the $CaCl_2.6H_2O$. The freezing point of the molten solid, after purification, was 29°.88. Since no value for its latent heat could be found in the literature, K for $LiNO_3.3H_2O$ was determined directly by experiment, using glycol, with the following result: 2.101 grams of glycol (M = 62) in 100 grams of molten $LiNO_3.3H_2O$ depresses the freezing point from 29°.88 to 29°.00, *i.e.*, 0.880°, from which K = 26.0. This value of K gave very satisfactory results for all the substances employed.

Using the value K = 26.0 in the formula $K = \frac{0.02\ T^2}{w}$, and solving for w, we find the latent heat of fusion of $LiNO_3.3H_2O$ at its freezing point 29.88°, to be 70.6 gram calories per gram.

$Na_2CrO_4.10H_2O$. The preparation of this salt gave much more trouble than the others, as the anhydrous salt separates if the solution is heated above 30°. It was possible, however, by infecting an overcooled saturated solution of Na_2CrO_4 with a crystal of $Na_2CrO_4.10H_2O$ to obtain a salt which had a freezing point of 19.92°. This is the salt we have used as solvent, though owing to the apparent existence of other less stable forms, freezing in the same neighborhood, it is not easy to obtain.

MOLECULAR WEIGHTS IN SOLUTION.

In $CaCl_2.6H_2O$ as solvent. K. = 45.0.

Grams per 100 of solvent.	Depression of freezing point.	Molecular weight.
I.—*Glycerol*[1] (92)		
3.160	1.58	90.
5.484	2.74	91.
6.962	3.46	91.
7.864	3.73	87.
9.590	4.91	88.
13.425	7.26	83.
II.—*Urea*[2] (60)		
0.891	0.595	67.
1.185	1.185	66.
3.860	2.560	65.
III.—*Glycol*[3] (62)		
2.633	1.640	70.
3.300	2.153	68.
5.341	3.345	72.
IV.—*Potassium Chloride*[4] (74)		
0.292	0.181	73.
0.702	0.423	75.
V.—*Calcium Bromide*[5] (200)		
0.371	0.087	192.

[1] Kahlbaum's "Special K."

[2] Kahlbaum's C.P., unpurified.

[3] Museum specimen.

[4] Kahlbaum's C. P., recrystallized three times.

[5] Prepared from Iceland spar and pure hydrobromic acid.

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The value of K here, also, was found by experiment, using sodium nitrate as the dissolved salt, for work on the other two solvents had shown that the ionization of a dissolved salt, when it has an ion in common with the solvent, is prevented. 0.9016 grams of $NaNO_3$ ($M=85$) in 100 grams of molten $Na_2CrO_4.10\,H_2O$ depresses the freezing point 0°.408, from which $K=38.5$. This value of K in $w=\frac{0.02\,T^2}{K}$ would lead to 44.5 calories as the heat of fusion of 1 gram of $Na_2CrO_4.10\,H_2O$ at its freezing point, 19°.92. Although this value of K gives fairly satisfactory results for other substances, we cannot express the confidence in it that we have in the others.

In more concentrated solutions the freezing point is higher than that of $CaCl_2.6H_2O$, due possibly to the separation of $CaBr_2.6H_2O$.

VI.—*Hydrochloric Acid*[1] (36.5)

Grams per 100 of solvent.	Depression of freezing point.	Molecular weight.
0.347	0.421	37.
0.438	0.605	33.
0.861	1.181	33.

VII.—*Potassium Nitrate*[2] (101)

0.596	0.520	51.
1.513	1.198	56.
1.564	1.180	58.

VIII.—*Ethyl Alcohol*[3] (46)

0.2652	0.21	57.
1.0958	0.89	56.
1.8550	1.32	63.
3.5057	2.21	71.
4.2900	2.47	78.
5.2140	2.85	82.
7.2292	3.40	96.
9.2517	3.83	109.
11.4259	4.26	121.
13.5912	4.68	131.
19.6313	5.57	158.
25.2080	6.47	175.

IX.—*Acetic Acid*[4] (60)

1.041	0.63	74.
1.388	0.84	74.
1.975	1.20	75.
2.878	1.46	92.
13.034	4.99	121.
16.440	5.74	131.
22.180	6.68	150.
33.680	8.67	174.

X—*Formic Acid*[5] (46)

1.146	1.00	52.
5.288	4.11	58.
8.647	6.12	64.
8.844	6.18	64.
14.775	9.58	69.

[1] Pure dry HCl was passed into the solution in the freezing tube, and titrated after the freezing point had been observed.
[2] Kahlbaum's c. p., not further purified.
[3] Kahlbaum's absolute.
[4] Kahlbaum's "Special K."
[5] " " "

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In $LiNO_3.3H_2O$ as solvent K = 26.0

XI.—*Glycol*[1] (62)

Grams per 100 of solvent.	Depression of freezing point.	Molecular weight.
2.101	0.880	62.
3.553	1.500	61.
4.153	1.811	59.
6.107	2.620	60.
22.120	9.880	58.

XII.—*Erythrite*[2] (122)

1.102	0.261	110.
2.350	0.640	95.
3.610	0,963	98.
3.983	1.020	101.
7.007	1.821	100.

XIII.—*Acetone*[3] (58)

0.898	0.400	58.
3.644	1.511	63.
4.075	1.642	65.
8.020	2.870	73.

XIV.—*Mannitol*[4] (182)

0.412	0.062	174.
1.529	0.220	180.
1.842	0.281	171.
3.011	0.450	174.

XV.—*Methyl Alcohol*[5] (32)

0.939	0.781	31.
3.277	2.550	33.
5.819	4.230	35.
7.023	4.810	37.
13.825	8.730	43.

XVI.—*Ethyl Alcohol* (46)

1.953	1.040	48.
5.356	2.461	56.
8.704	3.320	68.
9.040	3.500	07.
17.136	5.042	88.

XVII.—*Acetic Acid* (60)

2.700	1.160	60.
4.310	1.791	62.
5.631	2.262	62.
8.486	3.118	70.
8.974	3.180	73.

[1] Same sample as used in $CaCl_2.6H_2O$.

[2] 5 grams of this sample in 100 grams of *water* depressed the freezing point $0^C.765$, which leads to M = 121.

[3] Kahlbaum's not further purified.

[4] 1.832 grams of this sample in 100 grams of *water* depressed the freezing point $0°.160$, which leads to M = 178.

[5] Kahlbaum's absolute.

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XVIII.—*Lithium Bromide*[1] (87)

Grams per 100 of solvent	Depression of freezing point.	Molecular weight.
1.492	0.441	88.
1.585	0.480	86.
2.570	0.782	86.

XIX.—*Potassium Nitrate* (101)

1.262	0.318	102.
1.717	0.440	101.
2.037	0.521	101.

XX.—*Potassium Chloride* (74)

0.304	0.200	39.
3.545	2.760	33.

XXI.—*Hydrochloric Acid* (36.5)

0.321	0.48	18.5
0.642	1.00	17.7

XXII.—*Lithium Chloride*[2] (42)

0.7864	0.50	41.
1.3487	0.88	40.

XXIII.—*Cadmium Chloride*[3] (183)

0.430	0.071	158.

In $Na_2CrO_4.10H_2O$ as solvent. $K = 38.5$[4].

XXIV.—*Urea* (60)

0.670	0.434	59.
1.340	0.841	61.
2.017	1.192	65.

XXV.—*Glycol* (62)

0.7360	0.434	65.
1.9577	1.078	70.
6.7100	3.640	71.

XXVI.—*Glycerol* (92)

1.672	0.720	90.
4.541	1.891	93.
10.736	4.370	95.

XXVII.—*Sodium Chloride* (58)

1.006	0.622	62.

The Molecular Weight of Water.

Water in all three solvents gave peculiar results by the ordinary method, although in each case analysis showed no abnormality in the solid phase separated.

By the Richards method[5], in $CaCl_2.6H_2O$, the following results were obtained.

[1] Prepared from pure $Li\ CO_3$ and HBr.

[2] Prepared from pure $Li\ CO_3$ and HCl.

[3] Kahlbaum's, not further purified. No stronger solutions could be made.

[4] In getting these results we were assisted by Mr. J. S. Mills.

[5] This Journal, 25, 291 (1903). Using a mixture of solid $CaCl_2.6H_2O$, in presence of its pure liquid phase, and finding the depression of the equilibrium point after the addition of varying amounts of water, analyzing a sample after each reading.

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XXVIII.—*Water* (18)

Grams per 100 of solvent.	Depression of freezing point.	Molecular weight.
3.80	0.82	24.
4.40	0.82	17.
8.00	2.32	21.

Higher concentrations than these caused the freezing point to rise, even though the water added had a temperature of 10° below that of the system.

Effect of Infection of Molten $CaCl_2.6H_2O$ with a Crystal of $CaCl_2.2H_2O$.

If the over-cooled molten $CaCl_2.6H_2O$ is infected with a crystal of $CaCl_2.2H_2O$ in place of one of the hexahydrate, a solid phase is separated at a lower temperature, *i.e.*, at 26°.80. If to this system a crystal of the hexahydrate is added, the temperature at once rises to the value 29°.48. This would indicate, contrary to the conclusion of Roozeboom[1], that $CaCl_2.2H_2O$ can exist as a solid, in presence of the liquid phase, below 60°, for analysis of the solid phase at 26°.80 showed this composition.[2]

Discussion of Results.

It will be seen from the foregoing results that as found by Löwenherz for molten $Na_2SO_4.10\,H_2O$; molten salts, containing water of crystallization, when employed as solvents for the freezing point method, behave very much as does water, with the exception that they reduce or drive back completely the ionization of dissolved salts, when these have an ion in common.

Just as in water solutions we find in many cases an apparent increase in the molecular weight with the concentration, so here the alcohols and and acetic acid in molten $CaCl_2.6H_2O$ and $LiNO_3.3H_2O$ lead to values which, by the ordinary method of calculation, are decidedly abnormal, and which increase in abnormality with increased concentration. Before attempting to draw conclusions from these results, it will be necessary to decide whether they really are abnormalities, or only apparent abnormalities, due to a common and mistaken use of the freezing point law when applied to higher concentrations.

In the usual derivation of the freezing point law the assumption is made that either the heat of dilution is zero, or that the solution is so dilute that the addition or removal of solvent is accompanied by no appreciable heating or cooling effect. Hence if one of these conditions is not fulfilled, it is certainly not correct to conclude that the results are abnormal; and it is absurd to attempt to explain their assumed abnormality by assuming changes within the system itself.

Bancroft[3] has shown by thermodynamical reasoning that the osmotic

[1] Z. physik. Chem., 4, 31 (1889.)
[2] This point will be further investigated.
[3] J. Physic. Chem., 10, 319, (1906).

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pressure of a solution must vary with the magnitude and sign of the heat of dilution, *i.e.*, when heat is evolved on dilution, we may expect to find an abnormally high osmotic pressures; and vice versa. It can also be shown, thermodynamically, on this assumption, that the freezing point depressions of solutions which absorb heat on solution and dilution should be smaller throughout than those calculated by aid of the usual formula; in other words for the determination of the molecular weight, the depressions observed should be compared to a smaller value of K than the usual uncorrected one. This would cause the molecular weights, so calculated, to be lower than those found by the usual formula; and, as the heat of dilution would be the greater, the greater the concentration, the magnitude of the correction to be applied to the calculated molecular weight would also be the greater, the stronger the solution. As solutions of acetic acid or alcohol in molten $CaCl_2.6H_2O$ or $LiNO_3.3H_2O$ absorb considerable heat on dilution we suggest that this may be the explanation of the increasing molecular weights found for them above; for it is conceivable that such a correction would lead to molecular weights for these substances which are independent of the dilution, as they appear actually to be from the determinations of Morgan and Benson, based on the coefficient of distribution. As the necessary data are not as yet at hand for the testing of such a formula quantitatively, we offer this theory as a tentative explanation for the discrepancies of this sort found here and elsewhere, leaving the actual quantitative application of it to a later date.

Summary.

I. Molten salts, containing water of crystallization, may be used as solvents for the freezing point method, and lead to molecular weights similar to those observed in water, except that the ionization of the substance dissolved, when it has an ion in common with the solvent, is decreased or prevented.

II. The freezing point constants for $CaCl_2.6H_2O$, $LiNO_3.3H_2O$, and $Na_2CrO_4.10\,H_2O$ are respectively 45.0 ($m.p. = 29°.48$); 26.0 ($m.p. = 29°.88$); and 38.5 ($m.p. = 19°.92$).

III. The latent heat of fusion of $LiNO_3.3H_2O$, calculated from the experimentally determined freezing point constant and the formula $K = \frac{0.02\,T^2}{w}$, is equal to 70.6 gram calories per gram, at the freezing point 29.88°.

IV. Acetic acid and the alcohols, in both $CaCl_2.6H_2O$ and $LiNO_3.3H_2O$, by the freezing point method, show increasing molecular weights with increasing concentration. It is suggested that this is due to the heat absorbed when these solutions are diluted.

LABORATORY OF PHYSICAL CHEMISTRY,
June, 1907.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY NO. 141].

DETERMINATION OF MOLECULAR WEIGHTS BY DISTRIBUTION EXPERIMENTS[1].

By J. LIVINGSTON R. MORGAN AND H. K. BENSON.

Received June 11, 1907.

According to Nernst[2] and Aulich[3] and others[4] it is possible to find the relation existing between the molecular weights of a substance in two immiscible solvents by distributing it between them. The simplest derivation of this law is the following:

Assume the formula of a substance to be A in one solvent, and A_n in the other immiscible one, where n is equal to 1, or greater. The chemical reaction in the two-layer, heterogeneous system, then, will be

$$nA = A_n$$

and the application of the law of mass action will lead to the relation $\frac{C_{An}}{C_A^n}$ = constant, where C_{An} and C_A are the concentrations in moles, per unit of volume, of the substances A_n and A in the two layers.

This constant is of course independent of the single values of C_{An} and C_A, and dependent only upon the temperature.

If $n = 1$, the substance being a gas which is distributed between a liquid and a space above it, we have Henry's law, *i. e.*, $\frac{C_{\text{as gas}}}{C_{\text{in solution}}}$ = constant. When $n = 2$, as is the case when the solvents are water and benzene, and the substance benzoic acid, it is found that $\frac{C^2_{\text{water}}}{C_{\text{benzene}}}$ = constant, at any one temperature and independent of the total amount of benzoic acid present in the system.

In place of concentration, *i. e.*, moles per liter, we can employ grams per unit volume. Thus, since $C_1 = \frac{w_1}{M_2}$ $C_2 = \frac{w_2}{M_2}$, and $M_1 = nM_2$ we find that — constant$=C_1/C_2^n$ —can also be written in the form$((M_1/M_2^n)$ constant$) = w_1/w_2^n$, where w_1 and w_2 are the grams in the two layers per unit of volume. In other words, so long as at all dilutions M_1/M_2^n is a constant, we can use w_1/w_2^n in place of C_1/C_2^n. *And, conversely, if w_1/w_2 is a constant for all dilutions, M_1 must be equal to M_2.*

[1] Abstract from the Dissertation (Columbia 1907) of H. K. Benson.

[2] Z. physik. chem., **8**, 110, (1891).

[3] Ibid, **8**, 105, (1891).

[4] See Hantzsh and Sebalt, ibid, **30**, 268, (1896); Hantzsch and Vagt, ibid, **38**, 705, (1901); Roloff, Ibid, **13**, 341. (1894); Jakowkin, Ibid, **20**, 19, (1896); Hendrixson, Z. anorg. Chem., **13**, 73, (1897); Riecke, Z. physik. Chem., **7**, 108, (1891); H. Fischer, Dissertation, Breslau, (1905); Herz and Lewy, Z. electrochem., **11**, 818, (1905) and others.

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The substances studied in this investigation were those which absorb heat on dissolving, and show variation in the molecular weight with the concentration, according to the freezing point method; together with those which were necessary to interpret these. The results of the distribution experiments, expressed in grams per cc., are as follows:

I. ACETIC ACID BETWEEN WATER AND ETHER.

W_w	W_e	$\frac{W_w}{W_e}$
0.0044	0.0025	1.76
0.0200	0.0101	1.98
0.0694	0.0370	1.88
0.0768	0.0364	2.11
0.1152	0.0616	1.87
	Average	1.92

II. ACETIC ACID BETWEEN MOLTEN $CaCl_2.6H_2O$ AND ETHER.

W_s	W_e	$\frac{W_s}{W_e}$
0.0124	0.0175	0.709
0.0216	0.0285	0.757
0.0249	0.0358	0.696
0.0518	0.0767	0.675
0.0933	0.1229	0.759
0.1298	0.1940	0.669
	Average	0.711

III. ACETIC ACID BETWEEN MOLTEN $LiNO_3.3H_2O$ AND ETHER.

W_s	W_e	$\frac{W_s}{W_e}$
0.0092	0.0072	1.28
0.0216	0.0194	1.11
0.0261	0.0249	1.05
0.0533	0.0508	1.05
0.0869	0.0869	1.00
	Average	1.09

IV. ETHYL ALCOHOL BETWEEN WATER AND ETHER.

W_w	W_e	$\frac{W_w}{W_e}$
0.0116	0.0164	0.707
0.0289	0.0496	0.583
0.0543	0.0833	0.652
0.0660	0.1157	0.570
0.0689	0.1127	0.611
0.102	0.1896	0.538
	Average	0.610

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V. ETHYL ALCOHOL BETWEEN MOLTEN $CaCl_2.6H_2O$ AND ETHER.

W_s	W_e	$\frac{W_s}{W_e}$
0.0039	0.00387	1.01
0.025	0.0247	1.01
0.025	0.0210	1.19
0.0388	0.0332	1.14
0.0463	0.0369	1.26
0.098	0.0764	1.27
	Average	1.15

VI. ETHYL ALCOHOL BETWEEN MOLTEN $CaCl_2.6H_2O$ AND BENZENE.

W_s	W_b	$\frac{W_s}{W_b}$
0.288	0.0382	7.54
0.4566	0.0606	7.53

VII. ETHYL ALCOHOL BETWEEN WATER AND BENZENE.

W_w	W_b	$\frac{W_w}{W_b}$
0.040	0.0385	1.04
0.0693	0.0683	1.02
0.160	0.1316	1.22
0.262	0.1936	1.36

Equal volumes of the two solvents were used throughout, in each case the system being agitated at 25° until equilibrium was established. The acetic acid was titrated with a standard base, using phenolphthalein as indicator. The content of alcohol in the two layers was found by the Method of Thorpe and Holmes[1]. 25 cc. of the layer were removed and placed in a separating funnel, diluted to 100 cc. with water, saturated with sodium chloride and mixed with 40 cc. of petroleum ether. After shaking for five minutes the layers were allowed to separate and the lower one withdrawn for distillation. The layer of petroleum ether was washed several times with saturated salt solution and the washings added to the main portion. The latter was next distilled through a Hopkins head and condenser into a 50 cc. flask, protected against evaporation by an adapter. The flask, after distillation had continued until one-fourth of the original solution had distilled over, was filled to the mark with distilled water. To determine the alcohol in grams in this distillate, the specific gravity was determined by aid of a Sprengel-Ostwald pycnometer and from that, by means of the conversion table of Morley[2]; the percentage of alcohol by weight determined. This weight was the amount of alcohol present in the original 25 cc.

Discussion of Results

Before using ether as the second solvent it was necessary to find the molecular weights of alcohol and acetic acid, when dissolved in it. As

[1] J. Chem. Soc., 83, 314, (1903).

[2] This Journal, 26, 1185. (1904).

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these cannot be found by aid of the freezing point, and since solute, as well as solvent, distils when heated the boiling point method is not applicable, there is no direct method. The method used was as follows: The molecular weights of ethyl alcohol and acetic acid in water have been determined up to high concentrations[1]; and increase but slightly with increased concentration. Solutions of acetic acid and ethyl alcohol in water were shaken with equal volumes of ether, and gave (see tables I and IV) practically constant results, within the experimental error. Tables II, III, and V also show constancy in the ratio for acetic acid between ether and $CaCl_2.6H_2O$ and $LiNO_3.3H_2O$, and alcohol between ether and $CaCl_2.6H_2O$. This proves, then, that acetic acid and alcohol have practically the same molecular weights in ether as they have in water (which is nearly independent of concentration, as shown by the freezing point method); and that this molecular weight is really the same as that in molten $CaCl_2.6H_2O$, notwithstanding that the freezing point leads, according to Morgan and Benson, to absurd figures at high concentrations. Further, according to the coefficient of distribution the molecular weight of alcohol in benzene, (table VII) even ignoring the experimental error, does not vary as greatly with the concentration as it does according to the freezing points of Beckmann[2], who finds the value $M = 318$ for a solution containing 32.45 grams of alcohol to 100 of benzene.

Throughout, of course, all consideration of ionization has been omitted, for in all cases considered it is negligible, as compared with the experimental error; and simplicity rather than great exactness was thought important.

Summary.

I. The molecular weights of ethyl alcohol and acetic acid in ether are the same as in water, *i. e.*, $\frac{C_w}{C_e}$, for both acetic acid and alcohol is constant and independent of dilution.

II. The molecular weights of alcohol and acetic acid in molten $CaCl_2.6H_2O$ and in $LiNO_3.3H_2O$. derived from the coefficient of distribution, are the same as in water, although freezing point measurements, according to Morgan and Benson, using the ordinary formula, lead to absurd values in concentrated solutions.

III. The molecular weight of alcohol in benzene, derived from the coefficient of distribution, apparently does not vary with the concentration to such a great extent as it does when derived from the freezing point method.

LABORATORY OF PHYSICAL CHEMISTRY,
JUNE, 1907.

[1] Jones and Murray, Am. Ch. J., 30, 205, (1903).

[2] Z. physik. Chem., 2, 728, (1888).

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THE MERCURY MINERALS FROM TERLINGUA, TEXAS: KLEINITE, TERLINGUAITE, EGLESTONITE, MONTROYDITE, CALOMEL, MERCURY.[1]

W. F. HILLEBRAND AND W. T. SCHALLER.

In the late fall of 1905 the senior author received for identification from Mr. H. W. Turner, at that time connected with one of the mining companies of Terlingua, Texas, specimens of two minerals from the well known Terlingua mercury field in Brewster county. One of these proved to be the unidentified mineral referred to as No. 5 by Professor A. J. Moses in his paper[2] on new mercury minerals from that district, namely terlinguaite, eglestonite and montroydite, the last of these being mercuric oxide, the others oxychlorides. Preliminary tests having shown that No. 5 belonged to the so-called mercury-ammonium compounds, hitherto unknown in nature, a brief announcement[3] of this fact was made in order to secure the field for as full an investigation of this unique mineral and its associates as the material on hand and to be obtained might permit.

This work has been conducted at intervals during the past eighteen months, and is yet incomplete with reference to the new mineral. It has, however, extended over so long a time and the chances for obtaining more perfect material than that already available are so slight, that it is deemed inadvisable to longer delay publication of the results obtained. The full details of the work herein summarized will be found in a bulletin of the U. S. Geological Survey, the appearance of which will unfortunately be delayed still longer, chiefly on account of the plates that are to illustrate it and the unavoidable delays attending publication. Although the present condensation reproduces the essential points as to the chemistry of the minerals, it but touches their crystallographical side, which, though of much interest for the great number of forms shown by most of the minerals, requires too extended treatment for a resumé of this character. Further, many observations of interest that cannot be detailed here were made, upon which some of the conclusions were based, particularly in studying kleinite the mercury-ammonium compound. For these as well as the details of crystallography and association reference must be made to the full report.

A few words, however, with reference to their association as observed by us are necessary in this place. The minerals are deposited on a matrix of two kinds, first a soft, siliceous-aluminous, earthy mass, sometimes gray but usually of a pinkish color and containing a small amount

[1] Condensed from a forthcoming bulletin of the U. S. Geological Survey. Chemistry by Hillebrand, crystallography, etc., by Schaller.

[2] Am. J. Sci., [4] **16**, 253 (1903).

[3] Science, **22**, 844 (1905); J. Am. Chem. Soc., **28**, 122 (1906); Am. J. Sci. [4], **21**, 85 (1906).

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of calcium carbonate, and second, a fairly pure layer of calcite with large scalenohedral crystals projecting from the surface. The general associations of the several minerals are given below, but there are many exceptions that will be noted in the full report. Kleinite is found with gypsum, calcite, seldom with barite and calomel, either loose or on a whitish, clayey gangue, only once or twice accompanied by terlinguaite; calomel with calcite, mercury and eglestonite on the pinkish earthy gangue; eglestonite with calomel, calcite and mercury on the pink gangue or on calomel; montroydite with calcite, terlinguaite, and mercury on the calcite layer; terlinguaite with calcite, montroydite and mercury on the calcite layer.

Several members of this group of minerals are characterized by a most unusual property, namely, proneness to change color rapidly on exposure to light. With respect to terlinguaite and eglestonite this change is of a permanent character, and the result is to impart to the minerals an appearance often quite different from that they originally possessed. With kleinite the change is not to a different color but only to a different shade, and it persists only as long as the exposure itself, the original color returning in the dark. From published and privately communicated statements it would seem as if these minerals, in their earthy forms at least, must be difficult to distinguish as a rule when first found, by reason of the similarity of their original colors, all more or less pronouncedly yellow.

In addition to the specimens first received from Mr. Turner, many fine ones were donated by Mr. J. H. Hartley, who was also connected with one of the Terlingua mining companies, and later Mr. R. M. Wilke, of Berkeley, California, gave kleinite when more was needed. All was, so far as known to us, from the properties of the Marfa and Mariposa Mining Co., and chiefly from the Terceiro shaft. Professor A. J. Moses kindly identified the new mineral with his No. 5, and sent us his original measurements of the latter. To these gentlemen, and especially to Mr. Hartley for his most generous liberality, also to Dr. P. G. Nutting, of the Bureau of Standards, and Prof. B. B. Boltwood, of New Haven, who kindly made certain tests, we take occasion to express our deep sense of obligation.

In the several descriptions that follow we have incorporated data already correctly given by Professors Moses and Sachs, as well as the new matter gathered by ourselves, in order to present as complete a record as possible of the minerals described. In general due recognition is given of observations made by others, though it may not have been possible in every case.

Kleinite.

Before describing the unique compound referred to in the foregoing it

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will be necessary to impose on the reader a little history. On the day preceding the appearance in Science of the announcement regarding the new mercury-ammonium compound there was read at a meeting of the Royal Prussian Academy of Sciences a paper by Professor A. Sachs, of Breslau, descriptive of an oxychloride of mercury which was regarded by him as perhaps identical with the No. 5 of Professor Moses, and to which he assigned the formula $Hg_4Cl_2O_3$, or $3HgO.HgCl_2$, and the name kleinite, after the eminent mineralogist Prof. Carl Klein. This paper appeared in print[1] on Jan. 11, 1906. After reading the announcement of the mercury-ammonium mineral, said to be also identical with the above No. 5 of Professor Moses, Professor Sachs made new analyses of material in his possession and obtained results[2] agreeing qualitatively in each case and quantitatively in one with those which had already been obtained in Washington. His later data appear in the table below:

	Sulphur-yellow Crystals		Orange Crystals
Hg			85.29
Cl			6.97
SO_3	1.05	0.85	2.57
NH_3	0.44	1.09	2.79

He regarded the sulphur-yellow crystals as the purer, and from the varying values for sulphur and nitrogen argued that these could not be integral components of the mineral. Without committing himself to any view as to the molecular arrangement, the following formula was suggested as the most plausible — $Hg_4(Cl.\frac{1}{2}SO_4)_2\ [O,(NH_2)_2]_3$ — which is of the same type as his original oxychloride, $Hg_4Cl_2O_3$, but is far from being in close agreement with his analytical data and is also opposed to the chemical behavior of the mineral as a mercury-ammonium compound. The assumption by Professor Sachs of hydrogen, and of oxygen other than that in the SO_4 radicle, was purely arbitrary, and it may be said here that his surmises as to the formula of the mineral have not been verified by the results of our work, nor have we found any certain difference in composition between the light yellow and the orange crystals.

It had been the intention of the senior author to assign to the mineral a name indicative in some manner of its composition when this should have been fully established, but to now substitute for the name kleinite, already in the literature even though applied to an incorrectly identified species, another name, no matter how appropriate, would occasion confusion that it is desirable to avoid; hence the name kleinite is accepted without reserve.

Physical Properties. Most of the material as received was in loose crystals or crystal aggregates, to which adhered more or less of a dull earthy white to reddish foreign matter of a clay-like character. While

[1] Sitzb. kgl. Preuss. Akad. Wiss., 1905, 1091-1094.
[2] Centralb. Min. Geol. Pal., 1906, 200-202.

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many of the crystals were very fine and brilliant much of the material was far too impure for the chemical tests that were contemplated. Even the selected crystals and aggregates held here and there a little of the gangue firmly attached and some must also be included in the crystals themselves in an extraordinarily fine state of division, to judge both from microscopic evidence and from the amount of non-volatile matter that was left on ignition, which ranged from about 0.75 to nearly 3 per cent. This gangue interfered much with the correct determination of the water given off by the mercury mineral on heating and hence with the establishment of a formula.

A peculiarity not noticed by other observers is that when exposed to sunlight or even to the diffused light of a room, after having been in the dark, the crystals, at first canary yellow, almost immediately became much deeper in color, generally reddish yellow or orange, but that they regained their original color very soon when again placed in the dark. This phenomenon could be reproduced as often as desired. It was also noticed that the exposed crystals were not all of the same shade of yellow; there were some that had not changed at all and others that showed all gradations between almost colorless and orange, and one crystal was seen with an orange core and a light outer zone. Professor Sachs also noticed different shades in the same crystal. In powder the color is sulphur-yellow. One of the first specimens received was composed entirely of very pale yellow, coherent crystal masses held together by or holding together a reddish earthy gangue. The lighter crystals that were picked out for separate analysis from samples of the loose crystals varied in color, but all were much lighter than the rest in daylight.

The density was determined on several specimens and found to average for the orange crystals 7.975 and for the light yellow 7.987, but the results are all low because of the attached or included earthy matter. These figures are much higher than the 7.441 given by Sachs. The crystal form is hexagonal; $c = 1.6642$ (mean of Schaller's and Sachs' values). The habit is short prismatic, rarely equidimensional. (Fig. 1.)

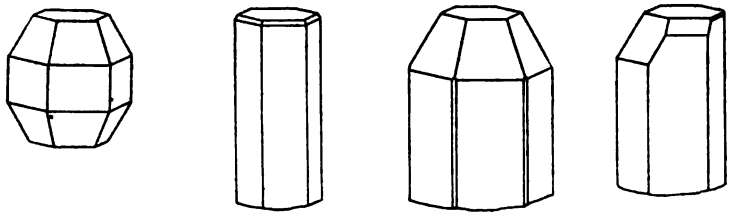


FIG. 1.—Crystals of Kleinite Showing Variation in Habit.

Single crystals rarely exceed one millimeter in length, but masses of crystalline material may exceed one centimeter. Five forms

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have been observed namely, $c\{0001\}$, $m\{10\bar{1}0\}$, $a\{11\bar{2}0\}$, $p\{10\bar{1}1\}$ and $x\{10\bar{1}2\}$ (new). Cleavage is good parallel to $\{0001\}$ and imperfect parallel to $\{10\bar{1}0\}$. Brittle. Luster adamantine to greasy on bright surfaces. Hardness apparently slightly over 3.5. Not radioactive (Boltwood), but Nutting reported faint evidence of helium on first warming the mineral in a vacuum.

The mineral being geometrically hexagonal a basal section should remain dark under crossed nicols. But, as described by Moses, such a section does not remain dark but shows double refraction and if thin enough will be seen to be composed of innumerable individuals, none of which is large enough to show interference figures. The double refraction is strong, the colors being of the third and higher orders. At about 130° the double refraction begins to decrease, as seen by the descending colors, until finally it becomes zero and the mineral remains dark under crossed nicols. The section now gives a uniaxial, positive interference figure. After cooling, the section remains dark but after the lapse of many months is seen to be slowly returning to its doubly refracting condition. This phenomenon seems to show that kleinite is dimorphous and that the uniaxial optical state agreeing with its outward hexagonal form is stable only above 130° approximately, while below that temperature its stable condition is biaxial, probably triclinic. According to this the hexagonal crystals of kleinite must have been formed at a temperature not much if any below 130°. As is stated just below, it is at a point but a few degrees higher than this that the first permanent browning of the mineral becomes visible when it is heated, and that considerable loss of water has then taken place. What connection, if any, there may be between these two phenomena is not known.

Pyrognostic Behavior. When carefully heated in a closed tube, or better in one through which passes a slow current of air, the mineral loses a little water, begins to brown at 135°-150°, and as the temperature rises becomes still darker and yields more water, but gives no visible sublimate under 260° even after several hours. Between 260° and 280° mercury and calomel (not $HgCl_2$) sublime. When most of the calomel has passed off the residue begins to grow lighter colored, then yellowish and finally becomes nearly white. During the expulsion of the calomel some gas (Cl ?) is evolved in minute amount that sets free iodine from solution of potassium iodide. On heating to 400° more of this active gas is evolved, but it is soon followed or accompanied by one that destroys the color of the free iodine (SO_2 ?). At 400°-420° appears a further sublimate less volatile than the calomel. If the test is made in a closed assay tube this last sublimate and the still unvolatilized residue may melt to a dark reddish liquid, which on cooling

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solidifies with a yellowish and then white color. Ammonia turns both sublimates black instantaneously, although the latter one often contains mercuric as well as mercurous sulphate. Most of the nitrogen escapes in the elemental state during the formation of the calomel, but not quite all. There is not the least evidence of the formation of ammonia. If the heating is carried out *in vacuo* the evolution of the active gas is much more marked than at atmospheric pressure and if collected by a pump is seen to be of the color of chlorine. Under the vacuum this gas does not act on the mercury of the pump, but fouls that in the collecting tube strongly under atmospheric pressure. The scum on the mercury gives tests for chlorine. This liberation of free chlorine was at first supposed to indicate direct union of nitrogen and chlorine in the mineral, but since it is also given off on heating *in vacuo* a mixture of the artificial compound $NHg_2Cl.xH_2O$ with a sulphate of mercury ($3HgO.SO_3$ in the test) it is evidently a secondary reaction between one of the products of breaking up of the radicle SO_4 and vapor of calomel or of the still undecomposed chlorine constituent of the mineral.

Behavior Toward Liquid Reagents. Soluble in warm hydrochloric as well as nitric acid without deposition of calomel. Also soluble in sodium sulphide and in ammonium bromide. The latter liberates as ammonia for every one part of nitrogen derived from the mineral itself three parts from the reagent. Fixed alkalies do not liberate ammonia. Hydrogen sulphide blackens speedily, ammonia not at all.

Additional Data. Several tests were made by decomposing the mineral *in vacuo* under varying conditions of treatment in order to get evidence as to the presence of either hydrogen in addition to that which was afforded as water or of oxygen other than that in water and the SO_4 radicle. For the evidence on these points reference must be made to the full report; suffice it to say here that no certain evidence was obtained in favor of the presence of one or the other of these elements other than in the combinations above named, though the proof is not absolute that there may not be small amounts of one or both (See also p. 1188). If present, the hydrogen is in such small amount as to be unimportant in the formula of the mineral as a homogeneous unit, and oxygen must also exist in all probability as basic oxygen in a minor constituent of a mixture. The summation given on p. 1188 is a strong argument against the presence of considerable percentages of either.

When, however, the mineral is fully decomposed by heat in presence of lime or sodium carbonate oxygen is liberated in quantity. Theoretically the amount should be exactly equivalent to the SO_4 and Cl_2 found in a particular sample if the compound is normal and not basic, and this should afford an exact means for deciding the question of the presence of oxygen. But as a matter of fact the oxygen never did equal the

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calculated amount by several tenths of one per cent. Of the various possible explanations to account for the deficiency the following, based partly on qualitative tests, seems the most probable. The oxygen is liberated partly in an active state, and forms a chloroxy-salt of sodium or else nitrite or nitrate of sodium in small amount. It would require but little of one of these salts to bind enough oxygen to account for the observed deficiency. The evidence favors an oxy-salt of nitrogen in preference to one of chlorine. It is, of course, assumed that any such salt was formed by the act of decomposition and did not pre-exist in the mineral.

Analytical Methods Employed and the Results.—(1) Nitrogen. For nitrogen three methods were used: (*a*) expulsion as ammonia by sodium sulphide and gravimetric determination as the chlorplatinic salt; (*b*) expulsion as ammonia by ammonium bromide in a closed vessel, collection of the ammonia in titrated oxalic acid and determination of the acid left over; (*c*) direct determination as nitrogen gas expelled *in vacuo*, collected by the aid of a Töpler pump, and measured in a gas burette after freeing from other gases if present.

Numerous data are to be found in the full report relating to these methods, particularly the last. The second method was found to yield about two-tenths per cent. more nitrogen than the first or than the second, when sodium carbonate was used as a retainer for the chlorine and sulphur, the results by which agreed well. This was probably in part if not altogether due to the action of the clayey gangue on the ammonium bromide with liberation of some ammonia (see p. 1188). Were it not for this effect of the gangue the method would be an excellent one for obtaining proof as to the presence or absence of basic oxygen. The nitrogen found by the third method was finally tested by passing it over hot magnesium, which absorbed apparently the whole of it. It was also tested spectroscopically. The analytical results were as follows calculated to gangue-free substance, the modes of decomposition employed being indicated at the heads of the several columns:

NITROGEN PERCENTAGES BY DIFFERENT METHODS.

Na_2S	HCl	Gas-volumetric		NH_4Br
		With Na_2CO_3	Without Na_2CO_3	
2.56	2.57	2.53	2.61	2.78
2.57		2.55	2.74	2.76
2.55		2.60	2.67	2.74
2.55		2.58	2.86	2.70
		2.43		
Aver., 2.555		2.54		2.74

The single determination after solution of the mineral in hydrochloric acid and removal of the mercury as sulphide and of the SO_4 as the barium salt, is regarded with confidence, as also those by the sodium sulphide

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method. The greater variation among the results by the gas-volumetric tests with sodium carbonate is to be ascribed to the small amounts of mineral used—0.25—0.5 gram,—the uncertainty in the burette readings in the upper section of the instrument and the greater chance for loss or gain during the numerous manipulations. The high results by the ammonium bromide method have been explained above. Those by the gas method without sodium carbonate are not clearly accounted for, but the results obtained in that way were always less satisfactory by reason of the fouling of the pump outlet and of the mercury in the collecting tube by the free chlorine that was formed.

(2) Mercury. Mercury was determined in several ways, almost always in connection with one of the nitrogen determinations: (*a*) As mercury, by ignition with sodium carbonate and once as in organic combustion of mercury compounds. Most of the determinations were by this method. (*b*) As mercury, by electrolysis from sodium-sulphide solution. (*c*) As the sulphide. The last method usually afforded higher and probably truer results than the first.

(3) Chlorine and sulphur. Since slight loss of chlorine and of sulphur as sulphur dioxide almost always resulted when the mineral was heated by itself, these components were determined in the sodium carbonate employed for the gas-volumetric determination of nitrogen. A greater variation among the few chlorine results for the lighter colored crystals was observed than for the orange-colored ones, which latter afforded excellently agreeing results. But the results for the lighter crystals were in no case so markedly different from the others as to confirm Professor Sachs' conclusion that there was an appreciable chemical difference between the crystals of different shades, and they were in part affected by obvious errors.

(4) Water. None of the water afforded by the mineral is hygroscopic. About one-half comes off at 135°–150°, and the total that is obtained by careful heating of the mineral by itself to complete decomposition, using a plug of gold leaf in the exit of the tube, is not clearly in excess of that obtained after the manner of organic combustion with copper oxide preceded by lead chromate and a roll of copper. Some of it comes from the clayey gangue, but most is beyond question given off by the mercury mineral. How much belongs to one and how much to the other it has been impossible to ascertain. The water determinations constitute the least satisfactory portion of the analytical results.

In the different specimens analyzed the gangue ran from 0.75 to 3 per cent. in the dehydrated state, as obtained by ignition. In the full report the many analyses are given both as made and after recalculation to a gangue-free basis for both orange and light colored crystals. We reproduce here only the averaged results for the deeper colored crystals since

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they were in best agreement, repeating that although the light colored crystals afforded greater variations in chlorine and sulphur than the orange ones, this was in part due to obvious errors, and that the means for these constituents were slightly higher than for the orange crystals, rather than far lower as found by Sachs. To include them would hardly affect the general average.

AVERAGE COMPOSITION OF ORANGE CRYSTALS OF KLEINITE.

Hg	85.86	÷	200	= 0.4293	=	2.34
Cl	7.30	÷	35.45	= 0.2059	=	1.42
SO_4	3.10	÷	½ 96.06	= 0.0646		
N	2.57	÷	14.01	= 0.1834	=	.1
H_2O	1.03	+	18.02	= 0.0571	=	0.311
	99.86					

In discussing the above ratios, it must be borne in mind that the number for water is of doubtful value, so that it can receive little attention. The water cannot exist in large part even as hydroxyl, for that would require an amount of basic oxygen entirely opposed to all the evidence, in which that of summation is not of least import. The ratio shows at once that there is far too little nitrogen for a general formula of the type $NHg_2X.xH_2O$, in which X represents Cl and SO_4. It is even insufficient for the chlorine alone in such a formula, and we are therefore obliged to consider the possibility of the body being a mixture. Calomel as a constituent of such a mixture is excluded from consideration for the reason that but a trace is indicated on dissolving the mineral in warm hydrochloric acid, and this appears to be derived from the gangue. Mercuric chloride would seem to be excluded by its solubility in water. As oxychlorides there would naturally be considered first terlinguaite and eglestonite, but both are excluded for the reason that they yield on solution in hydrochloric acid calomel. It remains to assume a mercuric oxychloride and then an oxysulphate, both of which might perhaps be formed simultaneously with $NHg_2Cl.xH_2O$, from a mercuric solution containing more mercury than is needed by the ammonia present to form a compound of this type. If perchance the oxychloride were Hg_2Cl_2O or $HgO.HgCl_2$, and allowance were made for it on this basis in the ratio above given, the ratio of the residuals would show an oxysulphate with Hg to SO_4 as 4 to 3.23 and composition nearly $Hg_4O(SO_4)_3$, or $HgO.3HgSO_4$. The calculated amounts of these salts would demand 0.33 per cent. of basic oxygen, an amount that happens to coincide almost exactly with that indicated by the nitrogen determinations according to the ammonium bromide method (p. 1186), which as will be remembered gave more than was obtained by other methods. While the excess of ammonia obtained by the ammonium bromide method is with considerable reason believed to be in part due to the action of the aluminous gangue

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on the reagent, calculation shows that it cannot well all have originated thus. If not, the only alternative, assuming that the tests were reasonably correct, is that an oxy-salt or salts of mercury must have given rise to some at least of that excess of ammonia. The chief objection to accepting this alternative is the volume of oxygen corresponding to the required weight percentage, which if wholly given off as oxygen gas on heating the mineral itself ought not to have escaped detection and approximate measurement. Still, it is conceivable that in this method of operating the basic oxygen might not all escape as gas. The evidence as to the presence of a little basic oxygen is conflicting, and further speculation would be profitless in the present state of our knowledge regarding this remarkable mineral. To assume that the nitrogen is very low and should be 2.885 per cent. or exactly equivalent to the chlorine, is opposed by much evidence, including the fact that the sulphate would then be strongly acid.

It is regrettable that the long labor has resulted in nothing more definite than the fixing of this mineral as the first naturally occurring member of the so-called mercury-ammonium compounds and the untenableness of the possibility suggested by Professor Sachs. The question as to the structure of these mercury-ammonium bodies, whether they belong to one or other of the several types that have been suggested for them, is outside the scope of this investigation.

Montroydite.

Orthorhombic holohedral: $a : b : c = 0.6375 : 1 : 1.1977$ (Schaller). Fifty-six forms observed, forty-five new. Two crystal habits with all intermediate gradations: (1) Prismatic, flexible, dark-red needles, commonly 1½ cm., occasionally 2½ cm. long, by less than 1 mm. thick, often partially grayish from what appears to be a thin coating of some other (presumably mercury) mineral, or minute and orange in several forms, notably wormlike, and (2), nearly equidimensional crystals of a few millimeters diameter. The larger needles occur also in curiously twisted and curved shapes, the minute orange ones in irregular rounded and loosely coherent masses. There are also hollow, irregularly-shaped and bubble-like formations that in their interior resemble geodes, being lined with or nearly filled with one or both of the above-mentioned types of crystals. A somewhat different form of bubble is found between large calcite crystals, smooth and somewhat glistening exteriorly, gray-black and partially filled with a spongy mass of crystalline material that is commonly very dark in color. Precise descriptions of these and other modes of occurrence are difficult to give in few words.

Color, dark red to yellow-brown or orange-brown. Streak, yellow-brown. Transparent to translucent. Cleavage, perfect {010}. Hardness, 2–3, less than 2 (Moses). Brittle, also sectile, but the long needles

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extremely flexible, can be rolled around a thin rod. Density not determined because of inability to separate completely from free mercury enough for a satisfactory test.

Completely volatile without fusing, yielding in a closed tube a sublimate of mercury only. Slowly blackened by hydrogen sulphide, but not equally over all surfaces.

Since the oxygen as given for montroydite by Professor Moses was assumed by difference, a direct determination was made by dissociating the mineral *in vacuo*, collecting, measuring and testing the gas evolved. The result was to confirm the identification of Professor Moses.

ANALYSIS OF MONTROYDITE.

	Theory HgO	Found in 0.2213 g.	
Hg····	92.59	92.74	weighed as metal
O ·····	7.41	7.49	calculated from the volume.
	100.00	100.23	

Terlinguaite.

Monoclinic prismatic (holohedral), $a:b:c = 1.6050:1:2.0245$, $\beta = 74° 23'$. (Schaller.) Of the one hundred and thirty-three forms observed, one hundred and two are new. Crystals often extended in one direction and also equidimensional. The largest crystal measured 16x4x4 mm., though faces over a centimeter broad are sometimes to be seen. Also occurs in powdery form impregnating the earthy gangue, to judge from the greenish color of some specimens of ore, and perhaps in a similar state admixed with eglestonite, in which case its identification is at least difficult. Much confusion seems to exist as to the original color of terlinguaite before it has been exposed to light. Moses writes of it as "sulphur-yellow with a slight greenish tinge, very slowly darkening on exposure to an olive green," but Mr. Hartley in reply to our inquiry wrote that the terlinguaite crystals were green ere they were touched by the sunlight, but that most of the terlinguaite occurs as a yellow powder changing to green. Sometimes brown crystals are seen and occasionally the green and brown colors appear in the same crystal. When brown they are difficult to distinguish at sight from eglestonite in one of its transitional color stages. Some of our earthy specimens that were yellow at first turned greenish on exposure and presumably contained terlinguaite. Beautiful spots of emerald green reflected light appear when the crystals are examined with a lens as they occur on the specimen. If at times originally yellow the mineral is not in that state always distinguishable from kleinite, and perhaps not from eglestonite or even from the orange-red form of montroydite.

Streak yellow, turning greenish grey in light. Transparent or nearly so. Luster, brilliant adamantine. Cleavage, perfect $\{\bar{1}01\}$. Brittle to subsectile. Hardness, 2–3. Density, 8.725 (Moses).

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The effect of heating crystals in a closed tube differs somewhat according as this is done slowly or quickly. When quickly done there is violent decrepitation, continuing till the mineral has volatilized, the substance turning red-brown or almost vermilion in color (orange-yellow cold) and much of the resulting powder being projected up onto the sublimate of calomel and mercury above the assay. Eventually there is complete volatilization. With slow heat decrepitation is hardly noticeable. With the first burst of calomel sublimate there appears a little mercury, but then only calomel so long as there is any chlorine left in the residue. Sometimes at the last, when the flame is removed, brilliant short red needles of mercuric oxide form on the warm glass by recombination of some of the mercury vapor and oxygen.

In vacuo the color changes of the crystals as the heat increases are more marked, these being, after first appearance of a sublimate, red, black (without loss of luster), red-brown, orange-brown and dull. Before becoming completely orange-brown some faces are olive-greenish. When orange-brown the only visible sublimate is calomel and no trace of oxygen has been evolved. The residue then seems to be mercuric oxide, upon the decomposition of which partial recombination of its constituents occurs, to judge from the deposition on the warm glass near by of a slight orange-brown sublimate.

Hydrogen sulphide blackens the edges of a crystal, but further action is very slow; ammonia blackens only after some time. The second test serves to distinguish the mineral from eglestonite, which is at once blackened by ammonia. This difference in behavior of terlinguaite and eglestonite is in line with their chemical difference, the former being mercuric-mercurous, the latter wholly mercurous. Hydrochloric and nitric acids decompose terlinguaite with separation of calomel. The hydrochloric filtrate yields much bivalent mercury. Cold acetic acid slowly decomposes the mineral when in powder, also with separation of calomel, and in the filtrate hydrochloric acid produces no further precipitate, or but a very faint one. Eglestonite under similar treatment yields a heavy calomel precipitate, the filtrate from which is free from mercury.

Moses' empirical formula was confirmed by analyses in which the oxygen was measured directly and found to be wholly absorbed by phosphorus, thus showing its freedom from nitrogen.

ANALYSES OF TERLINGUAITE CALCULATED TO GANGUE-FREE SUBSTANCE.

	Theory Hg_2ClO	I.	II.	III.	Ratio of III.
Hg	88.65	88.92	88.31	88.61[1]	2.00
Cl	7.85			7.83	1.00
O	3.50			3.75	1.06
	100.00			100.19	

[1] Mean of I and II.

The high oxygen found in III is due probably more to error in meas-

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uring so small a volume as 2.67 cc. than to the little montroydite that was present.

The only artificial mercuric-mercurous oxychloride hitherto prepared[1] has the formula of terlinguaite.

Eglestonite.

Isometric holohedral. Crystals small, equidimensional, usually about and under one millimeter in diameter. They show two habits, one determined by the development of the rhombic dodecahedron and not particularly rich in forms, the other determined by development of the octahedron and with abundant forms. Of the twenty-one forms observed seventeen are new. Whether eglestonite can be distinguished by its color in the mine or soon after removal therefrom from terlinguaite, with which it is sometimes closely associated, or from kleinite or the orange montroydite, we are unable to say, but from the confusion that existed in the minds of those who sent us our specimens it seems that it must be at least difficult to do so. The first specimens received were dark brownish and of dodecahedral habit, others were of octahedral habit and light brownish yellow. These last became darker in time. If sufficiently exposed the crystals turn black, but without losing their luster, as noticed by Moses. Streak yellow, turning black. Luster adamantine to resinous. Transparent to translucent. Brittle. Cleavage lacking. Fracture uneven and apparently sometimes conchoidal. Hardness, 2–3 (Moses). Density, 8.237 (Moses); not determined by us for the same reason as with terlinguaite, difficulty of freeing perfectly from mercury enough material for a satisfactory test.

When heated in a closed tube, comports itself in almost every respect like terlinguaite. The residue, after expulsion of the calomel, seems to be mercuric oxide as with terlinguaite, formed in this case, however, from mercurous oxide at the expense of half the mercury of the latter, a reaction which accords with the observation that no oxygen escapes till all the calomel and some mercury have sublimed.

Hydrogen sulphide acts very much as upon terlinguaite and ammonia blackens at once, the latter reaction serving as a ready distinguishing test between the two minerals. Hydrochloric and nitric acids decompose it with separation of calomel. The hydrochloric acid filtrate contains no mercury. Cold dilute acetic acid acts more quickly on the powder of eglestonite than on that of terlinguaite, calomel is left and from the filtrate much more can be obtained by hydrochloric acid. The final filtrate is free from mercury. These tests, confirmed by the analysis, show clearly the mercurous nature of the compound, the first authentic instance of a mercurous oxychloride, native or artificial.

Analysis did not confirm the empirical formula $Hg_6Cl_3O_2$, deduced from

[1] Fischer, T., and von Wartenberg, H., Chem.-Ztg., **29**, 308 (1905).

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J. S. McCord's analyses in the paper by Professor Moses, a formula which, in fact, is invalidated by the qualitative data above given, since it calls for mercuric as well as mercurous mercury. The analyses were made in the main as for terlinguaite, with the exception that the chlorine and mercury in the sublimate were each time determined, the separation being effected by sodium hydroxide, and the little mercury that goes into solution with the chlorine by this operation being recovered. Calculated to gangue-free substance the results were as follows :

ANALYSIS OF EGLESTONITE CALCULATED TO GANGUE-FREE SUBSTANCE.

	Theory Hg_4Cl_2O	I. 0.1195 g.	At. ratio	II. 0.1008 g.	At. ratio	III. 0.1198 g.	At. ratio
Hg.....	90.21	88.33	4.11	88.94	3.87	89.73	3.99
Cl.....	7.99	8.32	2.18	8.23	2.02	8.12	2.03
O	1.80	1.72	1	1.84[1]	1	1.80	1
	100.00	98.37		99.01		99.65	

In all cases the mercury is probably low, and calomel was present to a slight extent in sample I at least. It is quite probable that the oxygen was less accurately determined than the chlorine, but the effect of low mercury and the presence of calomel are better brought out by the ratio based on oxygen than on chlorine as unity. The formula plainly indicated is Hg_4Cl_2O, or $Hg_2O.2HgCl$, one that is in full agreement with the qualitative behavior of the mineral. The variations in the analytical data reported by Moses are so wide that the excellent agreement of his averages with the formula $Hg_6Cl_3O_2$ can be d n uet oa lyo balancing of large errors. The oxygen values of his table were indirectly determined and are affected by the errors involved in other determinations, which inspection shows were large.

The ammonium bromide method, used with kleinite for determining nitrogen, might probably be employed successfully with eglestonite and terlinguaite and any other compounds of similar kind for the indirect but very accurate determination of the basic oxygen in them.

Two specimens of what was supposed to be eglestonite were analyzed, but with results indicative of a mixture of terlinguaite with calomel, though the appearance of both was decidedly against this. Possibly they represent a new species.

Calomel.

The crystals of calomel often reach a large size, some being 1 1/2 cm. in diameter. They are very rich in forms, a total of thirty having been observed, of which ten are new. The crystals are frequently twinned, twinning plane e { 011 }. The formula for calomel being well established, no chemical work was done on this mineral.

Native Mercury.

Native mercury occurs abundantly on nearly all of the specimens, ex-

[1] 1.90 by loss in weight of ign. tube.

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cept those of kleinite, on which we have not seen it. It is usually present as globular irregular masses associated directly with the other minerals. Globules often project from small cavities on the surfaces of crystals of terlinguaite, eglestonite and montroydite, and are sometimes to be seen in the interior of crystals of terlinguaite and montroydite, notably the latter. While much of it is in the form of a fairly pure liquid, a good deal is mixed with powdery oxychlorides as a sort of stiff paste having a gray or greenish color and irregularly associated with the plainly crystallized oxychlorides and montroydite. The proximate determination of this gray or greenish mass is almost impossible. Some of the mass has a yellowish, almost metallic sheen, which is perhaps largely an iridescent effect.

Summary.

Kleinite, as announced in 1905, belongs to the so-called mercury ammonium compounds, but no probable formula can be deduced from the analyses. It may be a mixture of a mercury-ammonium chloride in great preponderance, $NHg_2Cl.1/3H_2O$, with an oxychloride and sulphate or oxysulphate of mercury.

Terlinguaite is a mercuric-mercurous oxychloride, HgO.HgCl, the formula of Moses being confirmed and the mixed nature ascertained by tests.

Eglestonite is a mercurous oxychloride, $Hg_2O.2HgCl$, the first authentic instance of such a compound, either artificial or native, and not $Hg_6Cl_3O_2$, as believed by Moses.

Montroydite is mercuric oxide, as supposed by Moses, and proven now by direct determination of its oxygen content.

LABORATORY U. S. GEOLOGICAL SURVEY,
Washington, D. C., July.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 139.].

SOME NEW DOUBLE PHOSPHATES OF CHROMIUM.[1]

BY LOUIS J. COHEN.

Received June 10, 1907.

In attempting to prepare a double phosphate of chromium under the conditions of acidity already described in the formation of the iron and aluminum salts,[2] negative results were obtained; no precipitate was formed even when an extremely large excess of diammonium phosphate was added. When, however, the acidity was diminished, a precipitate was readily obtained.

The chromium solution employed was prepared by treating a little more than twenty grams of Kahlbaum's chromium hydroxide with 45.2

[1] Read at the April meeting of the N. Y. Section of the Amer. Chem. Society.

[2] This Journal 29, 5.

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cc. of hydrochloric acid (1.2)[1]. After slightly warming, the volume was made up to 500 cc., thoroughly mixed, allowed to stand and finally filtered from the undissolved hydroxide. The resulting clear solution was acid to litmus and contained approximately six grams of chromium chloride in 100 cc.

As it was impossible to previously determine the acidity required to form a double phosphate, four precipitations were made yielding respectively the products "A," "B," "C," and "D," referred to below, from solutions containing varying amounts of hydrochloric acid; the total volume in each case being 400 cc.

As the method of preparation was the same for all, a detailed description of one will suffice.

Sample A. A solution consisting of 100 cc. of the chromium chloride solution, 90 cc. of water and 10 cc., of hydrochloric acid (1.2), was heated to 80°. To this was gradually added, with constant stirring, 50 grams of diammonium phosphate dissolved in 200 cc. of water. The green precipitate which first formed was gelatinous in character, but on heating on an asbestos pad, for one-half hour, was observed to change at 90° to a dense and granular form, which rapidly settled, leaving a clear, slightly green supernatant-liquid. After digestion on a boiling water-bath for one-half hour the clear liquid was siphoned off and the residual compact mass washed by decantation with alcohol (1:1), containing 0.1 per cent. of ammonium chloride; and finally washed on a filter with alcohol (1:1) till free of chlorides; it was then dried in the water oven and analyzed. The supernatant liquid was acid to litmus, and gave a strong test for phosphoric acid and ammonia; showing that an excess of the precipitant had been added.

Sample B was prepared under the same conditions, except as regards acidity; which in this case was 15 cc.; in sample C, 1 cc. was used; with sample D no acid was added.

The filtrates from each of the last precipitates were slightly green, acid to litmus, and gave strong tests for phosphorus and ammonia, showing that an excess of the precipitant had been added.

There appeared to be scarcely any difference in the color of samples A, B and C, which were all light green.

Sample D possessed a bluish-slate color when first formed, which on continued heating acquired a violet tinge and finally on drying in the water oven became dark green.

Method of Analysis.—In the analysis of the chromium compounds, considerable difficulty was encountered in the determination of phos-

[1] This being the calculated amount of hydrochloric acid for the complete solution of 20 g. of the hydroxide.

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phorus. The usual method of separation with ammonium molybdate in a nitric acid solution, was incomplete; the ammonium phosphomolybdate invariably carrying down with it appreciable amounts of chromium, as was shown by its olive color. Precipitating in a larger bulk, followed by thorough washing with dilute nitric acid solution having failed to remove the contamination, reprecipitation was resorted to. This gave a more yellow precipitate, but this still retained chromium, as shown by the purple tint of its solution in ammonia, and by the slight color of the magnesium pyrophosphate obtained therefrom. Precipitation of the phosphorus with barium chloride in an alkaline solution, was next tried; but this method also failed to give a satisfactory separation. These methods were, therefore, abandoned, and those based on the preliminary oxidation of the chromium tried; after some experimentation the following method was adopted.

About one gram of the sample was treated in a beaker with a solution of sodium hydroxide (prepared from sodium) and warmed till complete solution took place. Sodium peroxide was then added in small amounts and the solution brought rapidly to a boil. After a clear yellow solution had been obtained, the boiling was continued for fifteen minutes, the solution was cooled, neutralized with sulphuric acid, transferred to a 500 cc. flask, and diluted to the mark. 50 cc. were pipetted out, diluted to 150 cc., and then made slightly alkaline with ammonia. The phosphorus was precipitated with magnesia mixture in the usual way and weighed as pyrophosphate. In the filtrate or in another 50 cc. the chromium was determined volumetrically by titrating with standard thiosulphate solution the iodine liberated. The ammonia was determined in the usual way.

On the assumption that the compound contained three molecules of water at the temperature of drying the analytical results were:

	Found Per cent.	Theory for $(NH_4)_2HPO_4 . 2\,Cr\,PO_4 . 3H_2O$ Per cent.
P	19.63	19.36
Cr	21.43	21.69
NH_4	7.55	7.52

The close agreement sufficiently warrants the supposition that at the temperature of drying, the salt retains three molecules of water, and has the composition represented by the formula.

Analysis of samples C and D gave results leading to the formula $5\,NH_4H_2PO_4 . 2\,Cr\,PO_4 . 4\,Cr\,(OH)_3$.

	Found D Per cent.	Theory for $5NH_4H_2PO_4 . 2\,Cr\,PO_4 . 4\,Cr\,(OH)_3$ Per cent.
P	17.24	16.93
Cr	24.43	24.38
NH_4	7.06	7.04

The reduction of the acidity therefore results in the formation of a

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basic double phosphate. On ignition all the samples decompose giving off water and ammonia. The double chromium phosphates differ from those of aluminum and iron in their non-formation from strongly acid solutions, their greater tendency to form basic salts and their ability to combine with the secondary ammonium phosphate.

The Double Phosphate of Chromium and Sodium.—$Na_2HPO_4 . 2 Cr PO_4$. From the results of experiments with diammonium phosphate upon hydrochloric acid solutions of the chlorides of iron, aluminum and chromium, it seemed quite probable that corresponding sodium and potassium salts could be prepared by substituting the disodium and dipotassium phosphates respectively for the diammonium salt. In the case of the double chromium phosphate, however, this supposition appeared to be contradicted by the work of the Bloxam[1], who, on boiling an acetic acid solution of a chromium salt with disodium phosphate, obtained a green precipitate which from the results of his analysis, he regards as a basic chromium phosphate retaining five molecules of water at 100°. He states that his product contained admixed impurities, but no mention is made of the nature and extent of the latter in the analytical results. The readiness with which these double phosphates hydrolyze when excessively washed with water, and it appears that Bloxam's product was so treated, and the fact that no mention is made of the absence of sodium in his product, seem to show that he first obtained a double phosphate of sodium and chromium which on prolonged washing with water changed to the basic compound he finally obtained and analyzed. This supposition is strengthened by the work of Steinschneider[2], who found that on excessive washing, with water his double phosphate of sodium and copper was converted to a basic phosphate, which was free from sodium.

Preparation.—To 40 cc. of the chromium chloride solution used in the previous preparations, diluted to 100 cc., sodium hydroxide was added until a slight but permanent precipitate formed; after clearing with a drop or two of acetic acid, 20 cc. more of 50 per cent. acetic acid was added and the resulting solution heated on an asbestos pad; 50 grams of disodium phosphate dissolved in 200 cc. of water were then gradually added with constant stirring and the volume made up to 400 cc. The resulting clear solution was then heated; no precipitate formed at first, but on continued heating a cloudiness soon formed followed by the formation of a green gelatinous precipitate which on further heating to 100° became dense; it was then transferred to a boiling water-bath for a half hour and allowed to stand over night. The next day the clear, colorless, supernatant liquid was siphoned off; it was found to be acid

[1] Chem. News, 52, 194-195.

[2] Uber die phosphates des Kupfers, Dr's Dissertation, p. 35.

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and gave a strong test for PO_4. The precipitate was washed twice by decantation with alcohol (1:1) then transferred to a filter and washed again with alcohol (1:1) till free of chloride; it was then dried in a water oven and analyzed.

The dried precipitate possessed a green color, considerably lighter than that of any of the chromium compounds already mentioned.

Analysis gave:

	Found Per cent.	Calculated for $Na_2HPO_4 2Cr PO_4 5 H_2O$ Per cent.
Cr	19.45	19.77
P	17.56	17.68
Na	8.79	8.75

These results fully confirm the supposition to which the results of Bloxam's basic chromium phosphate lead, *viz.*, that the addition of disodium phosphate to a solution of chromium chloride precipitates a double phosphate of chromium and sodium, which readily hydrolyzes on excessive washing with water to a basic phosphate.

In conclusion I wish to acknowledge my indebtedness to the late Prof. E. H. Miller for suggestions in the early stage of this work and also to express my thanks to Prof. H. C. Sherman, Prof. J. L. R. Morgan and Dr. F. Metzger for valuable assistance.

QUANTITATIVE LABORATORY,
April, 1907.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF TECHNICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 1.]

THE ANNEALING OF STERLING SILVER.

BY WM. H. WALKER.

Received May 29, 1907

It was early found by the workers in metallic silver that the ware made from an alloy of copper and silver was superior in almost every respect to that made from pure silver. Although quite a wide variation in the relative amounts of these two metals can exist and still produce a usable alloy, that proportion which has been accepted as a standard and which is called "Sterling" is composed of 7.5 per cent. copper and 92.5 per cent. silver. As is the case with other alloys, Sterling silver suffers a change in its physical properties when subjected to mechanical treatment such as rolling, drawing, stamping, etc., becoming hard, stiff and brittle. When the alloy is annealed by heating it to low redness, these undesirable properties doubtless due to molecular strains, disappear, and the ware may be subjected to further mechanical treatment. These frequent heatings produce on the alloy a scale of black copper oxide which so long as the articles were finished by hand was entirely removed by the subsequent filing and buffing necessary to produce the required polished surface. When the more modern methods of rolling and stamp-

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ing were introduced, a very much less severe treatment on the buffing wheels was necessary to produce the desired polished surface, and consequently the silver was removed to a very much less extent. Under these circumstances there appeared upon the finished ware a dark sheen or reflex which greatly diminished the luster and market value of the goods. This undesirable appearance is called by the workmen "fire surface" and is found to penetrate the silver alloy to a distance roughly proportionate to the number of times the alloy has been annealed. In order to remove this "fire surface" it is necessary to place the ware in strong nitric acid and dissolve away the alloy until the darkened portion has disappeared. This entails a loss to the manufacturer both from the silver dissolved and the danger of deep pitting due to the irregular action of the nitric acid.

A cause for the appearance of this black surface layer may be found in the supposition that copper oxide is formed within the silver alloy and that when the surface is polished, the minute segregated portions of copper oxide give rise to the "fire surface". As the depth of this blackened layer is at times very considerable, it is necessary to assume that the oxygen of the air penetrates the silver even at so low a temperature as 500° C. Although the solution of oxygen in molten silver has been carefully studied, the only reference to the absorption of oxygen by silver at low temperatures, found in the literature, is to the effect that below the melting point, no appreciable absorption occurs.

It required but a very simple experiment to prove that not only does Sterling silver absorb oxygen from the air but that this absorption commenced at a temperature below 500°. Of Sterling silver in the form of machine turnings, 10.2 grams heated in a glass tube in an atmosphere of oxygen, absorbed 135 cubic centimeters of the gas. The amount required to transform the copper present in the alloy into copper oxide was found by calculation to be 134 cubic centimeters.

The eutectic alloy of copper and silver has a percentage composition of 28 parts of copper and 72 parts of silver. Sterling silver, therefore, considered metallographically, may be looked upon as being composed of small bodies of the silver-copper eutectic imbedded in pure silver. If these portions of pure copper are converted into black copper oxide during the annealing process, they should be discernible when an annealed specimen is viewed under the microscope. Fig. 1 represents the polished cross-section of a fork tine which has been subjected a relatively large number of times to the annealing process. The depth to which oxygen has penetrated is distinctly shown by the dark patches of copper oxide-silver eutectic.

There is therefore no doubt as to the cause of "fire surface," and a process to anneal Sterling silver without the formation of this black layer

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must be one which can be carried on in an atmosphere containing little or no oxygen.

The most easily available artificially maintained atmosphere relatively free from oxygen is found in illuminating gas. A small annealing oven was therefore constructed in which could be maintained an atmosphere of carburetted water gas during the time the silver ware was exposed to the heat. The pigs or bars of Sterling silver were when in that form annealed in an open furnace, and when reduced to sheet metal the annealing was completed in this oxygen-free oven. The finished ware was found to contain no oxide. It had acquired, on the other hand, a peculiar velvety appearance which was removed with great difficulty when the article was polished. Examined under a microscope, this appearance was seen to consist of and be caused by minute blisters. When a piece of *pure* silver, that is, free from copper, was treated in a perfectly analogous way, no blisters were produced. Pieces of regular Sterling silver which had at no time been exposed when hot to an atmosphere containing oxygen, also showed no blisters. On the other hand, a piece of Sterling silver containing "fire surface" as shown in Fig. 1, after being exposed to the hot illuminating gas, largely lost its characteristic black band and appeared as in Fig. 2. It appears as if the hydrogen or hydrocarbon gases had penetrated the silver and reduced the copper oxide to metallic copper with the formation of water. This water vapor seems to have been unable to penetrate the silver and accumulating below the surface, caused the formation of the small blisters.

When ware annealed in this atmosphere of carburetted water gas was taken to the soldering room another difficulty was met. It may be said in explanation that hollow silver ware such as tea-pots, coffee urns, mugs, etc. are frequently decorated by soldering to the plain body, strips of silver beading or edgeing, by means of a small gas blow-pipe. It was found that wherever the tip of the oxidizing flame touched the ware annealed in the atmosphere of reducing gas, blisters were formed. The only explanation which I can assign for this phenomenon is, again, that water vapor is not able to penetrate silver as rapidly as can either hydrogen or oxygen. Hydrogen is doubtless excluded or adsorbed by the silver during the process of annealing, and when the oxygen carried by the blowpipe flame impinges upon the hot surface, it also penetrates the silver, and uniting with the hydrogen, forms water vapor, which owing to the pressure generated forms the blisters. This theory is further substantiated by the following fact— If a piece of this annealed ware be very slowly heated in the air and then soldered, no blisters appear. In this case the oxidation of the hydrogen takes place slowly and the water vapor is able to escape. If such a piece be rapidly heated, blisters of

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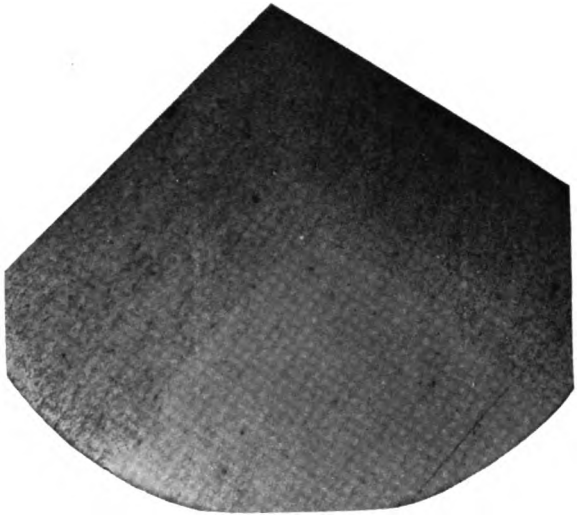


FIGURE 1

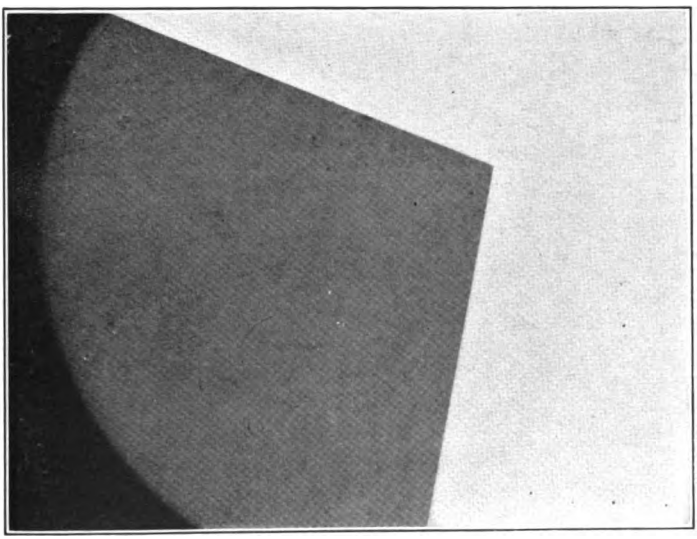


FIGURE 2

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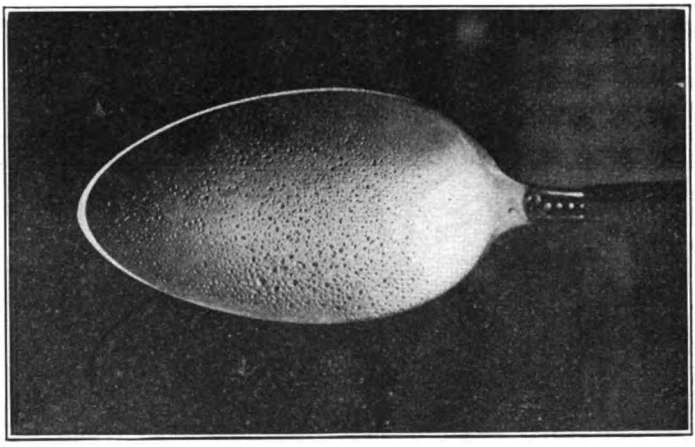


FIGURE 3

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very considerable size may be formed. Fig. 3 shows a spoon which has been annealed in water gas and then plunged into the tip of a large Bunsen flame. The figure is of the natural size.

It was thus made evident that in order to successfully anneal the ware, not only must the penetration of oxygen be prevented but also the penetration of reducing gases. Experiment showed that hydrogen, methane, acetylene, etc. were very active in producing blisters, while nitrogen and carbon dioxide were entirely inert. Carbon monoxide lay between the two extremes. Further work indicated that the most desirable atmosphere from a technical point of view was one which contained enough reducing gases such as hydrogen, methane, or carbon monoxide, to prevent the penetration of the small amount of oxygen which cannot be excluded when working with large furnaces, and enough inert gas, such as carbon dioxide or nitrogen, to prevent the penetration of the reducing gases. Such an atmosphere can be prepared in an apparatus such as is employed in making so-called producer gas, when so operated as to deliver a product consisting approximately of two thirds carbon dioxide and nitrogen and one-third carbon monoxide, with a small amount of hydrogen. Annealing processes based on the above observations are now employed in practically all the large silver producing factories in America.

I wish to acknowledge the constant interest and support in this work received from Mr. C. E. Cole, President of the Towle Manufacturing Company, Silversmiths, Newburyport, Massachusetts, and from Mr. Martin Boyle, sometime chemist of the same firm.

THE RAPID DETERMINATION OF NICKEL IN THE PRESENCE OF CHROMIUM, IRON AND MANGANESE.

By C. M. Johnson.

Received May 17, 1907.

In applying the method of T. Moore[1] to the determination of nickel in steel, the directions given on page 183, Analysis of Steel Works Materials by Brearley and Ibbotson were followed: One gram of steel was dissolved in a 150 cc. beaker with ten cc. of concentrated hydrochloric acid diluted with an equal volume of water.

When action ceased ten cc. of nitric acid (1.20) were added and the contents of the beaker were boiled to about one half. 16 cc. of dilute sulphuric acid were poured into the solution and also three grams of powdered citric acid. The solution was stirred until the citric acid was dissolved, transferred to a 600 cc. beaker, and rendered faintly but distinctly ammoniacal.

The nickel was titrated with a standard solution of potassium cyanide

[1] Chemical News, 72, 92.

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using a measured amount of standard silver nitrate and two cc. of a 20 per cent. solution of potassium iodide as an indicator. The deep red color of the citrate of iron greatly obscures the end point. The authors complain of this color and recommend the use of a condensing lens to cast a beam of light through the darkness. In the presence of chromium the writer found that a still more sombre gloom settled down over the close of the reaction. The authors mentioned, also state that this element retards the union of the cyanide and the nickel causing the recurrence of the cloud of silver iodide.

After struggling with the process for some time and always carefully separating the chromium, and with it the iron, in chrome steels, an attempt was made to dispel the darkness and also to avoid these tedious separations: Less citric acid per gram of steel was taken and the dark red shaded to blackness.

Naturally, the amount of citric acid per gram of steel was then increased, that is, six grams of citric acid per gram of steel were used and a marked improvement was noted. Still more citric acid caused a complete lifting of the shadows.

The following modified procedure was finally adopted for nickel steels after having been thoroughly tested with plain carbon steels to which known amounts of nickel had been added: Dissolve one gram of steel drillings in a 150 cc. beaker with 20 cc. of hydrochloric acid (1:1). When action ceases add ten cc. of nitric acid (1.20).

Reduce the volume of the solution to about 15 cc. keeping the beaker covered during the boiling. Remove the beaker from the fire and pour into it eight cc. of conc. sulphuric acid diluted with 24 cc. of water. The presence of the sulphuric acid is essential to a sharp end reaction between the cyanide standard and the silver iodide in the subsequent titration.

Transfer the contents of the beaker to one of 600 cc. capacity containing *twelve* grams of powdered citric acid. Stir until the citric acid is dissolved. Render this solution *faintly* but *distinctly* alkaline with ammonia, using one part of concentrated ammonia diluted with one part of water. A large excess of ammonia causes low results. Stand the beaker in running water until it is cold. The volume of the solution should now be about 300 cc. Much larger volumes than 300 cc. should be avoided as great dilution retards the end point causing the cloud of silver iodide to disappear and then to reappear again in a few minutes.

The faintly ammoniacal condition can be easily controlled by adding the ammonia rather slowly and noting the changes of color that ensue: The first change is to amber, then to yellowish green, then to distinct green, then to a light shade of green, then to a yellow almost matching

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the yellow color of the acid solution. The reappearance of the yellow tint indicates that alkalinity is nearly attained.

A little more ammonia now causes a brownish shade which is evidence that the ammonia is in slight excess. The moderately alkaline citrate of iron obtained in the proportion of one gram of iron to 12 grams of the citric acid yields a bright greenish yellow solution in plain nickel steels instead of being of a dense dark red shade!

To the cold solution, two cc. of a 20 per cent. solution of potassium iodide are added. From a 50 cc. burette a standard solution of silver nitrate is dropped into the same beaker producing with the iodide a white turbidity. The standard potassium cyanide is added with constant stirring until the cloud of silver iodide just disappears which it does on being converted into silver cyanide. Nickel cyanide is first formed and then the silver cyanide is produced:

$$(1)\quad Ni(NO_3)_2 + 4KCN = Ni(CN)_2.2KCN + 2KNO_3;$$

$$(2)\quad AgNO_3 + 2KCN = AgCN.KCN + KNO_3.$$

If the directions are followed as given, the titration can be accomplished at almost the full speed of the burette. If the titrated solutions are permitted to remain in the open beakers for a time a film usually appears on the surface of the liquid. No account is taken of it as its presence is most likely due to a superficial loss of ammonia. The reactions are always found to be completed when the body of the solution is freed of the iodide precipitate.

Standards—From the equations as given, 5.85 g. of silver nitrate are equivalent to 4.4868 g. of potassium cyanide. This weight of cyanide dissolved in one liter of water gives a value of one cc. equals about 0.001014 grams of nickel.

As comparatively little silver nitrate is needed with each analysis, it is not advisable to prepare more than a half liter of the water solution of this salt using 2.925 grams per 500 cc. of distilled water.

The potassium cyanide standard should contain about five grams of potassium hydroxide to the liter, which renders it quite permanent. The solutions are readily standardized by applying them to a plain steel to which a known amount of nickel has been added. The chemically pure double sulphate of nickel and ammonium is a convenient standardizing medium. For example 0.2 grams and 0.25 grams of the double sulphate can be weighed into 150 cc. beakers together with one gram of plain carbon steel drillings.

This mixture is then put through all of the foregoing manipulations and titrated with the cyanide solution that is to be standardized. The number of cc. of the silver nitrate and of the potassium cyanide solution used in this titration are noted. An excess of 10 cc. of the cyanide is now added and in turn titrated with the silver nitrate solution

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until a distinct cloud of silver iodide is produced. This second titration gives the relation between the silver solution and the cyanide.

An actual case will illustrate the calculations: In sample No. 3477, 1.7 cc. of standard silver nitrate solution were required to produce a distinct turbidity and also to combine with any excess of potassium cyanide standard. In all 35 cc. of the cyanide were consumed in the titration. When the cloud of silver iodide had just been dispelled an excess of 9.8 cc. of cyanide was allowed to flow into the clear solution. Just 10.1 cc. of silver nitrate standard were needed to produce a reappearance of the cloudiness. Therefore $9.8 \div 10.1 = 0.97$ or 0.97 cc. of cyanide standard solution equals 1 cc. of silver nitrate. Hence instead of deducting 1.7 cc. from 35 cc., 1.7×0.97 or 1.65 cc. were deducted leaving 33.35 cc. of cyanide combined with the nickel in this steel.

To a plain carbon steel 0.200 gram of double sulphate of nickel and ammonium were added put through all of the steps of a regular analysis. This mixture required 28.75 cc. of cyanide. The nickel salt contains 14.86 per cent. of nickel or $0.200 \times 0.1486 = 0.02972$ gram of nickel were present. Hence $0.02972 \div 28.75 = 0.00103$ or 1 cc. of standard cyanide solution is equivalent to 0.00103 gram of nickel. No. 3477 as has been stated required 33.35 cc. of the cyanide standard, and therefore, contains $0.00103 \times 33.35 = 0.03435$ or 0.03435 gram of nickel or 3.435 per cent.

Chromium-Nickel Steels.—When chromium is present proceed exactly as in plain nickel steels except that twenty-four grams of citric acid per gram of steel are used. This proportion of citric acid is adequate to render the end point quite as easy to see as in ordinary nickel steels. The action is prompt and free from recurrence of turbidity. Of course, cloudiness through the entire solution will occur, as the ammonia is dissipated from it, after it has stood for some time in an open beaker.

The tabulation (1) that follows furnishes satisfactory proof that chromium does not interfere with the successful technical estimation of nickel in its presence:

TABLE 1

Sample	No Chromium added Nickel found Per cent.	Per cent. of Chromium added to a portion of the same steels	Nickel found after the addition of varying amounts of Chromium
No 525	5.09	4.	5.10
2991	4.44	2.	4.45
7239	3.24	1.	3.28
3017	4.96	1.	5.03
612	3.47	0.5	3.47
7273	3.29	1.	3.31
622	3.56	0.5	3.56
7288	3.32	2.	3.41
7289	3.11	2.	3.16
663	3.57	6.	3.59
2991	4.44	3.	4.47

The chromium was introduced in the form of recrystallized chemically

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pure potassium dichromate. The dichromate crystals were mixed with a weighed amount of nickel steel drillings before the addition of the 20 cc. of hydrochloric acid. The combined action of the nascent hydrogen from the steel, the excess of boiling hydrochloric acid and the ferrous chloride reduced the chromate to chromic chloride, thus duplicating the conditions found when a chromium-nickel is similarly treated.

Determinations by this modification of the cyanide method can be finished in from 45 to 50 minutes, either in the presence or absence of any per cent. of chromium likely to be met with in steels or alloys soluble in the acids given. In this laboratory *duplicate* determinations in nickel or nickel-chromium steels are made in the time just specified. By the process one can decide in a few minutes whether or not nickel is present in a given steel and just how much. Tungsten, if present, does not interfere, appreciably, as has been noted by the authors mentioned in this article. The writer had two different amounts of nickel added to a steel containing several per cent. of chromium and 16–17 per cent. of tungsten. This steel was then carried through exactly as though no tungsten or chromium were present using the method as given for chromium-nickel steels.

Nickel added	Nickel found
0.0297 gram	0.0299
0.03715 "	0.0372
none	0.0006

Tests were then made in the same manner in the presence of molybdenum and vanadium as follow :

TABLE 2.

Name	Kind of steel or mixture	Nickel added Gram	Nickel found Gram
J. R. Steel	Contains 10 per cent. ± Mo	0.0297	0.0295
"	" "	0.0222	0.0223
"	" "	none	0.0002
Bxx–173 Steel	Contains 4 per cent. Mo and 4 per cent. Cr	0.0223	0.0222
"	" "	0.0297	0.0296
"	" "	none	0.0004
A mixture	0.920 Gram of Steel	0.0297	0.0298
	0.030 " " Nickel		
	0.018 " " Vanadium		
A mixture	0.840 Gram of Steel	.0223	0.0227
	0.022 " " Nickel		
	0.035 " " Vanadium		
A blank	1.000 Gram of Steel	none	0.0008
	0.035 " " Vanadium		

Table 2 demonstrates that neither vanadium, tungsten, chromium nor molybdenum, when present in the amounts given, interferes, appreciably in technical analysis. These amounts represent extreme cases, especially for the vanadium, it being equivalent in one instance to 3.5 per cent. V when one gram of steel is taken.

As copper also forms cyanides, its presence would cause results to be

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too high, but copper is religiously avoided in good steel making. Its presence is extremely unlikely in greater amounts than 0.06 per cent., although the writer, on one occasion, found as much as 0.25 per cent. in a low carbon steel, not a *crucible* steel, however. Crucible steel rarely contains over 0.04 per cent. copper. The choice brands are under 0.02 per cent. in copper.

Wishing to test the extent to which nickel could be titrated in the presence of large percentages of chromium, iron being also present, the mixtures as given in Table 3 were titrated with potassium cyanide. The various salts were weighed into 150 cc. beakers, together with the proper amounts of steel drillings. The same proportions of hydrochloric, nitric, citric and sulphuric acids were employed as are herein given for nickel-chromium-steels, and were applied in the same manner.

A sufficient quantity of the salts of chromium and nickel, and of the steel drillings were taken to give a total of one-half gram of metals in the mixture.

Double sulphate of nickel and ammonium ($(NH_4)_2SO_4.NiSO_4.6H_2O$), potassium dichromate and steel drillings free from nickel were used as sources of nickel, chromium and iron, respectively.

To obtain the nickel value of the cyanide standard under conditions similar to those existing in the mixtures tested, standardizing mixtures of these salts were prepared varying from the mixtures tested as much as 1 per cent. to 20 per cent. in the different constituents.

For mixtures exceeding 10 per cent. of nickel, a standard cyanide solution with a nickel value of 1 cc. = 0.0031 gram of nickel was used. The standardizing mixtures were dissolved and treated exactly as the mixtures tested. The same method of standardization was observed in the work recorded in Table 4.

TABLE 3.

Per Cent. of Metals.			Gram of Nickel.	
Ni.	Cr.	Fe.	Added.	Found.
30	40	30	0.1499	0.1494 ; 0.1495
60	20	20	0.2999	0.3003 ; 0.2989
20	40	40	0.1029	0.1022
5	90	5	0.0250	0.0248 ; 0.0244
4	92	4	0.0200	0.0199
1.5	95	3.5	0.00749	0.00805 ; 0.00822
0.5	99	0.5	0.00249	0.00225 ; 0.00243 0.00247 ; 0.0026
0	98.9	1.0	None.	None.

Table 3 demonstrates that nickel may be estimated by the foregoing modified cyanide process, using the proportions of citric acid as given, with sufficient accuracy for works analysis, and indeed for most practical purposes ; even when the percentage of chromium is as much as 99 per cent., and the nickel content is but one-half of one per cent.

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The titration of the mixtures given in Table 3, and containing the larger amounts of chromium, requires considerable practice on the part of the operator. The work should always be carried out in duplicate. The disappearance of the cloudiness in the presence of 0.100 to 0.450 gram of chromium in a volume of 350-400 cc., is much more exactly observed when the mixture containing the iodide cloud is compared, from time to time, with a *similar* mixture which is perfectly free of this milky turbidity. The dilution of the deep purple, or wine color, of these ammoniacal mixtures of citrates to more than 300 to 400 cc., renders the end point but slightly more distinct, and has the great objection of retarding the reaction between the cyanide and the nickel. The increase above twenty-four grams of citric acid, in the solution, even to the extent of adding sixty grams of citric acid, did not relieve the density of color to any perceptible extent.

When titrating with a standard, 1 cc. of cyanide = 0.0031 gram of nickel (three times the strength used for steels) do not also increase the strength of the silver standard to equal it, but still retain the silver nitrate standard as given for steels. A silver nitrate solution sufficiently concentrated to be equivalent, volume for volume, to the cyanide standard (1 cc. = 0.0031 gram of nickel) on being dropped into the solution containing the potassium iodide, does not produce the usual opalescence, alone, but also forms curds of iodide that do not readily combine with the cyanide standard. The end point is reached and the main body of the solution is free of cloud while curds of silver iodide still lie on the bottom of the beaker. The weaker silver nitrate standard, or 5.85 grams of silver nitrate to the liter, produces with the potassium iodide a finely divided cloud of precipitate that combines promptly with the strong cyanide standard, giving a sharp end point. Weigh, therefore, 2.925 grams of silver nitrate, diluting to 500 cc., and 13.4604 grams of the best grade of potassium cyanide, diluting to 1000 cc., for titrations of solutions containing from 0.100 to 0.300 gram of nickel; 1 cc. of this silver nitrate solution should be equivalent to 1/3 cc. of the concentrated cyanide standard (1 cc. cyanide = 0.0031 ± grams of nickel).

The titration of nickel by potassium cyanide in mixtures containing large percentages of manganese with varying amounts of chromium and iron was also tried.

As in the experiments outlined in Table 3, mixtures were prepared to contain one-half gram of metallic substances. The same nickel and chromium salts were employed. Potassium permanganate crystals supplied the manganese.

The crystals of double sulphate of nickel and ammonium, potassium dichromate and potassium permanganate, were weighed into a 150 cc. beaker with the steel drillings. To this were added 20 cc. of dilute hy-

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drochloric acid. The contents of the beaker were then boiled, after the first action was completed, until the chromate and permanganate were reduced. An addition of 10 cc. of nitric acid (1.20) followed, and the analysis was carried out exactly as given for chromium-nickel steels, using twenty-four grams of citric acid. The results obtained are given in Table 4. Sulphuric acid was added as in the process for steels.

TABLE 4.

Per cent. of Metals.				Gram of Nickel.	
Ni.	Mn.	Cr.	Fe.	Added.	Found.
41	20	10	30	0.2059	0.2058
20.6	40	20	20	0.1029	0.10228
15	60	15	10	0.0750	0.0752
1.5	95.5	1	2	0.00749	0.00762
0.25	94.9	2	2.9	0.00124	0.00122
——	94.9	2	4	None	0.00006

Table 4 gives evidence of the fact that nickel can be accurately determined in the presence of large percentages of chromium and manganese, if the conditions herein given are carefully observed. In the hands of a practised operator no difficulty was experienced in the analysis when as much as 95 per cent. of manganese was in solution with but 0.25 per cent. of nickel.

LABORATORY OF PARK STEEL CO. WORKS OF
THE CRUCIBLE STEEL CO. OF AMERICA.

THE DETERMINATION OF SILICA AND ALUMINA IN IRON ORES.

BY G. W. DEAN.

Received April 22, 1907.

Further experience with the method which was described in this Journal last year[1] has led to its modification in two or three important particulars. It has been found that the ore may be ignited directly instead of separating and igniting the residue from digestion with hydrochloric acid. It has also been found that a porcelain crucible is the most suitable for the igniton, since the ore is less liable to be overheated and the alumina rendered insoluble. When the determination of alumina is not required, the use of stannous chloride aids greatly in dissolving the ore. It has also been found that by heating the ore with sulphur it is partly reduced in such a manner that it is more easily soluble in hydrochloric acid and the whole method can be used when it is desired to determine both silica and alumina. The methods which are now used are as follows:

Determination of Silica Alone. Weigh 0.5 g. of the finely pulverized ore (100 mesh), transfer to a 20 cc. porcelain crucible, cover and heat over a Dangler burner until the contents of the crucible are dull red, raise the temperature for a few seconds and then remove the crucible from the source of the heat. The whole operation should take not more than two or three minutes. Transfer the ignited ore when cold to a beaker, add 20 cc. strong hydrochloric acid containing one gram of stannous chloride

[1] This Journal, 28, 882.

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in 225 cc. Boil vigorously until solution is apparently complete and for five or ten minutes longer. Twenty or thirty minutes will usually be enough. If the ore is very difficult to dissolve, a stronger solution of stannous chloride, or more of the same solution may be used. Dilute slightly, filter, and wash thoroughly first with dilute hydrochloric acid and then with water. Ignite and weigh the silica as usual.

2. *Determination of both Silica and Alumina.* Weigh 0.5 g. of the finely pulverized ore (100 mesh), transfer to a 20 cc. porcelain crucible and place on top 0.25 to 0.40 g. of sulphur, heat gradually until the ore is dull red and then raise the temperature slightly for ten seconds. Transfer to a beaker, pulverize the mass with a glass rod, add 25 cc. of hydrochloric acid and boil vigorously for fifteen minutes. Then add enough nitric acid to clear the solution and decompose the sulphides and boil vigorously for another five or ten minutes, repeating the addition of nitric acid and boiling if required. If dark particles remain undissolved after this treatment, it is probable that further treatment will not decompose them. Dilute, filter, wash and determine the silica, as before, and in the filtrate determine the alumina by any one of the various methods which are suitable. In this method the ignited mass is treated with hydrochloric acid first to gain the advantage of the reducing action of the hydrogen sulphide liberated from the sulphide of iron formed by the action of the sulphur. If the nitric acid is added at first, the advantage of this reducing action is lost and the oxides of iron are often very difficult to dissolve.

The methods have been applied to the determination of silica in the following ores: (1) Arizona hematite; (2) Wyoming low grade hematite; (3) Alabama limonite; (4) Alabama hematite; (5) Magnanite from Llano County, Texas; (6) Michigan Magnetite; (7) Michigan hematite; (8) Mesabi limonite; (9) Mesabi decomposed hematite; (10) Swedish hematite; (11) Swedish magnetite; (12) Highly aluminiferous hematite from Baraboo iron district; (13) Hematite from Port Arthur field in Canada; (14) Bog iron from Nova Scotia. The results are as follows:

	Determinations are in duplicate.		
	Per cent. silica by Na_2CO_3 fusion	Per cent. silica by Hydrofluoric acid method	Per cent. silica by above method
1.	12.06—12.20	12.08—12.10	12.09—12.13
2.	21.27—21.22	21.11—21.20	21.26—21.23
3.	13.77—13.68	13.69—13.72	13.73—13.62
4.	11.99—11.82	11.88—11.94	11.92—11.83
5.	14.28—14.33	14.32—14.31	14.36—14.41
6.	9.91— 9.99	9.82— 9.89	9.80— 9.81
7.	10.55—10.40	10.49—.. ..	10.50—10.52
8.	8.02— 8.00	8.15— 8.10	7.99— 8.08
9.	17.82—17.74	17.85—17.77	17.86—17.88
10.	7.09— 7.13	7.00— 7.04	7.06— 7.01
11.	6.72— 6.84	6.72— 6.67	6.74— 6.77
12.	31.12—31.18	31.09—31.12	31.08—31.11
13.	4.44— 4.52	4.40— 4.52	4.38— 4.40
14.	2.06— 2.05	2.08— 2.03	2.09— 2.00

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It is evident from the above that the method gives accurate results when applied to a great variety of ores.

EAU CLAIRE, WISCONSIN.

A NEW SHAKING DEVICE FOR THE CHEMICAL LABORATORY.

BY J. M. CAMP.

Received May 25, 1907.

Among the various pieces of apparatus going to make up the equipment of the modern laboratory, it is the purpose of this article to describe the latest appliance, in the shape of a shaking device. It was designed and is particularly adapted for the purpose of hastening the precipitation of phosphorus by the well-known and almost exclusively used molybdic acid method, and in the solution of steels or pig irons for carbon combustion. But it is equally useful where agitation is desired in a flask for either dissolving or precipitating. As can be seen from the photograph, it consists of a frame supporting a vertical shaft, which is revolved by a six-inch pulley wheel. The upper part of the shaft is bent slightly from the perpendicular. Encircling the bent portion of the shaft is a hub which in turn supports a flat disc on which the flasks to be shaken are attached. The hub and disc are prevented from turning, when the shaft is revolved, by suitable teeth on the underside of the hub meshing into corresponding teeth on the top of the supporting frame.

On revolving the shaft the motion of the disc is ideal for the purpose intended, and can be best likened to the simultaneous pitching and tossing of the deck of a ship in a tumultuous sea. With each revolution of the shaft a wave travels around the flask or flasks on the disc exactly as in hand shaking, and by increasing or diminishing the number of revolutions the number and intensity of the wave movement is controlled. To obtain the maximum agitation and still retain the solutions in the flasks, without corking, from one hundred to one hundred and forty revolutions per minute has been found satisfactory. The disc is made to hold six flasks, any one of which can be placed in or removed from the machine in a fraction of a second. The gripping device is movable, up or down, enabling it to be quickly adjusted to hold any size flask from a six ounce to a twenty-four ounce Florence or Erlenmeyer. The electrical power required to operate it is twelve hundredths of an ampere on 250 volts, about the equivalent of the one twenty-fifth horse power, or less than the average desk fan motor is consuming, so that with the proper counter shaft to give the desired number of revolutions, any source of power may be used.

Heat can be applied to the apparatus if desired by means of a circular

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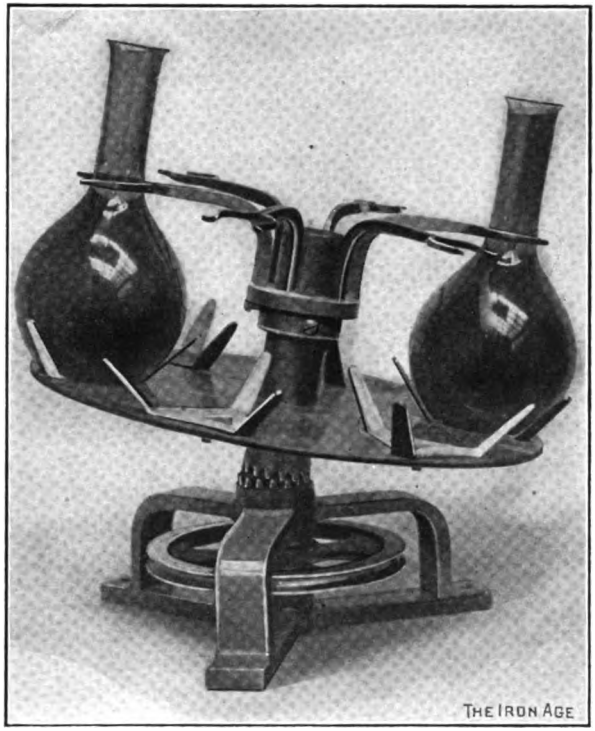


FIGURE 1

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burner, but it has been found that by adding the hot liquid to the flask, or heating the contents of the flask before placing it in the machine, the same end is obtained.

The advantages of the machine over hand shaking are to the chemist only too obvious. During the time of shaking the operator can be doing other more profitable work, with the assurance that aside from being relieved from the fatigue of the operation, the machine is not striking the job—as is the natural disposition of mankind—resulting in false analysis, while with the machine the reverse is the case, it is always allowed to do its full quota of work. Then under its constant conditions, in phosphorus precipitation for instance, a precipitate of like crystallization is always obtained, aiding materially its estimation by judging its bulk, as is the practice in most busy open hearth steel work laboratories.

Too much can not be said in praise of the machine, its simplicity, ease of operation, quietness, and the readiness with which the flasks can be placed in and removed from the apparatus, and the fact that the flasks do not need to be corked will commend it to any one.

Application has been made and the claims granted for a patent covering the ideas embodied in this machine.

DUQUESNE, PA.

METHOD FOR THE ESTIMATION OF METALLIC IRON IN THE PRESENCE OF ITS OXIDES.

By HENRY G. MARTIN.

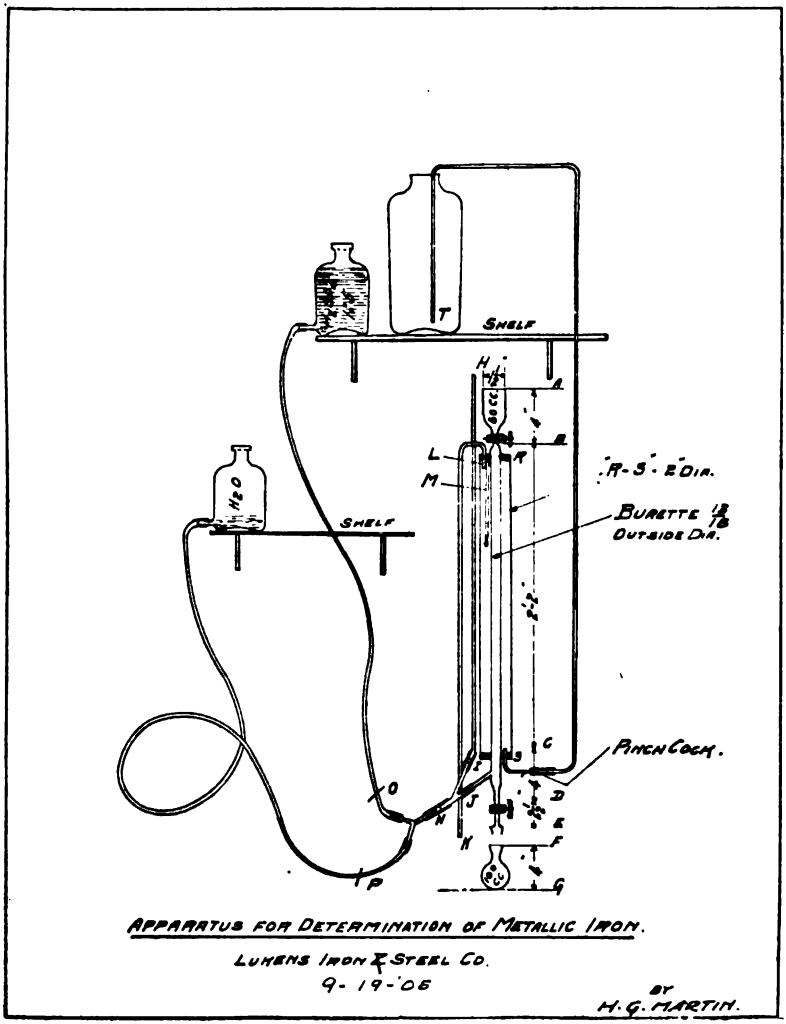
Received May 22, 1907.

For several years the writer has used the following method for the determination of the amounts of metallic iron, ferrous oxide and ferric oxide present in furnace products. The total iron is determined by solution, fusion of the insoluble residue, and titration. The sum of the ferrous iron and the metallic iron is determined by solution in dilute hydrochloric acid, with exclusion of the air and titration of the solution. And finally the metallic iron is determined by measuring the hydrogen evolved on dissolving the substance in dilute sulphuric acid. The method can not, of course, lay claim to strict accuracy, since it disregards the ferrous iron of the insoluble residue and also assumes that the ferric iron present is not acted upon by the hydrogen evolved during the solution of the metallic iron. If manganese is present, other errors may be introduced, and if the manganese content is high, the results are uncertain.

The hydrogen evolved by the solution of the metallic iron is determined as follows:

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The burette A-E is arranged according to G. Neumann and graduated in 1/5 cc. beginning at the stop-cock B. R-S is a water jacket supplied from a bottle on the upper shelf or from the hydrant. M is a small thermometer. R and S are secured by split wooden corks sealed with



cement made of litharge and glycerol. I, J, N, O and P are pinch-cocks. The burette at E is ground into the flask F-G. The bottom of the flask is about 8 inches from the table top and when in position under E is supported by wire gauze and an iron ring. D is a cock of quite large

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bore. The burette A-E together with three of the flasks, made interchangeable, were furnished by Geo. D. Feidt & Co. The remainder of the apparatus is home-made. S-T and L-K are of small bore; H-I should approximate the burette in bore.

Have the tube leading from the sulphuric acid bottle filled with the acid to its connection with the Y, then, with J and O closed, raise the water bottle until all the tubes are filled and the water has risen in the level tube H-I to near the top; close P, N and I, and open J, and set the water bottle on the lower shelf or on the table.

Weigh from 0.2 to 10 g., or more, of the material, according to the quantity of metal supposed to be present, into the flask F-G and fill to the neck with water and place in position on E; support it properly and place an argand burner under it with sufficient flame to boil the water, D and B both being open. Open I just enough to let a few cubic centimeters of water run into the burette. This will serve to completely fill the flask and tube D-E to above the cock D. When the water has boiled remove the flame for a moment. Open N and O until the sulphuric acid has filled the burette to B. Close B, then close O and open P simultaneously. As the action becomes less replace the flame and when all evolution has ceased, boil as at first, keeping the water bottle always lower than the surface of the liquid in the burette. Allow sufficient water to flow through the jacket to prevent any undue rise in temperature. Finally close D and remove the flask. Fill the funnel A-B with a moderately strong solution of potassium hydroxide and a few cubic centimeters of litmus solution. With the water bottle on the table, open B so as to allow the potassium hydroxide to flow into the burette very slowly. Allow it to run in until the liquid in the tube remains blue. This will remove any hydrogen sulphide or carbon dioxide. Most of the acid may be displaced with water before using the potassium hydroxide. Allow the apparatus to stand with the cooling water circulating until the temperature is the same as shown by the thermometer in the barometer near by. Open I, and with the thumb and finger on N, manipulate the water bottle until the liquid in the burette and that in the level-tube are at the same level. Observe reading. This reading is corrected from Liebermann's table to what it should be at 0°, dry, and 760 mm. pressure, equivalent to 1 g. of material, and multiplied by 0.002495 to find the value in terms of iron; $H = 1.008$; $Fe = 55.9$, one liter of hydrogen weighs 0.08987 g. The only error is due to absorbtion of hydrogen by the water and solutions used, and the apparatus may be standardized for this by making a determination with standard iron wire.

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This apparatus could also be used for making a determination of carbon dioxide from a carbonate.

LABORATORY OF LUKENS IRON AND STEEL CO.,
COATESVILLE, PA.

FURTHER OBSERVATIONS ON THE NATURE OF FECES FAT.[1]

BY J. H. LONG AND W. A. JOHNSON.

Received May 31, 1907.

In two earlier papers[2] figures were presented showing the amount of phophorus contained in the normal feces fat of a number of individuals. From the conditions of the experiments this phosphorus content, and the nitrogen found at the same time in one set of examinations, suggested the presence of a body or bodies of the "lecithin" type, using this term in the broader sense as describing the fat like "phosphatides" or "lecithans." Inasmuch as a lecithin content in feces fat has been frequently denied[3], while other authorities have maintained the reverse to be true[4], and have spoken of a high percentage amount of these bodies, it appeared that further work in this direction was desirable. In the following pages some observations on these and other points will be given.

For our experiments the mixed feces from a number of men in normal health were collected, dried and extracted with absolute ether, after rubbing up with fine ignited quartz. In the drying of feces in the ordinary way on the water-bath it is not possible to avoid the loss of some nitrogen, in non-protein combination, but the loss may be reduced somewhat by keeping the temperature low. On the other hand, the slow drying, with long contact with the air, occasions some change through oxidation processes. The loss of nitrogen from the fat-like bodies is the most serious of the objections to the water-bath method of drying, but in the working up of large quantities of feces it is practically the only method available and was followed, therefore, in our work.

By extraction in the Soxhlet apparatus we secured two lots of "fat" of about 40 grams each, which will be referred to as samples A and B. These crude fats were purified by solution in absolute ether, filtering and

[1] Presented at the New York meeting of the Am. Chem. Soc. Dec. 31st, 1906.

[2] Long, this Journal, **28**, 704. Long and Johnson, this Journal, **28**, 1499.

[3] Hoppe-Seyler, Physiolosische Chemie, p. 337. Hoppe-Seyler, Chemische Analyse für Aerzte, 6th Ed. p. 480. Bokay, Z. physiol. Chem., **1**, 157.

[4] For example, Deucher, Maly's Jahresber., 1898, p. 606. Also, F. Oefele, Maly's, Jahresber., 1904, p. 457.

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slow evaporation of the ether. There was a slight loss in this resolution in each case, possibly because the first extraction carried down traces of inorganic substances by aid of traces of water remaining in the dried feces. With the fat so secured, which was, of course, a mixture of all bodies present which are soluble in absolute ether, the following tests were made. Many of these tests were carried out on the purified fat and also on a fraction precipitated from its ethereal solution by acetone. The results from the original fat will be given first.

Experiments with Original Fat.

Sample A was used for most of the tests, and B mainly for confirmation. The two lots of fat are not absolutely comparable, but practically so in most respects, since they were obtained from the feces of the same individuals, with an interval of a few weeks between the collections.

Melting Point.—A constant melting point of such a mixture cannot be expected, from a consideration of the various factors which enter to modify it. Some of the single fats present are soft, with a low melting point, which cholesterol and the related koprosterol, which are always present in relatively large amounts, have high melting points, the first melting at 145° and the second at about 96°. The lecithin-like bodies have all a high melting point and when they are present the general consistence and behavior of the fat is greatly modified.

In our experiments with fat A the actual softening of the fat which could be designated as incipient fusion did not begin below about 65°, which value is higher than that usually quoted in the literature. The sample B showed even a higher fusion point, and not below 70°. The high melting point of crude feces fat depends not alone on the presence of cholesterol and other bodies mentioned above which may have their origin in the bile, but also on the nature of the fatty bodies of diet. When these fats are very hard with a high melting point their absorption is relatively imperfect and a considerable fraction may pass down the intestine to be lost with the feces, as was long since pointed out by Mueller[1] who showed also that the feces fat may have a melting point of 85° higher in the mean, than the melting point of the food fat.

Phosphorus Content.—The recognition of the phosphorus in the crude fat is a very simple matter, but the determination of the compound or compounds in which it occurs present greater difficulties. The practical difficulty is greatly increased by the fact that different methods of extraction yield crude fats with very different phosphorus contents, and when these are considered in relation to the nitrogen contents found at the same time, no uniformity can be found, as a rule, as will appear in the remarks on nitrogen content, below.

The many extractions we have made show that the amount of phos-

[1] See reference in Schmidts und Strasburger, "Die Faeces des Menschen," p. 149.

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phorus present in the crude fats from the feces of different individuals is extremely variable, but thus far no relation has been found connecting this amount with the diet or other factors. In our earlier papers referred to above, we noted in several crude fat samples amounts of phosphorus varying from 0.087 per cent. to 1.59 per cent. In the present case from fat A we found again a high phosphorus content of 1.17 per cent., which if calculated according to the old method to lecithin would correspond to about 30.5 per cent. of the distearyl product. On the other hand from fat B, which we expected to be in general similar to A, we found only 0.51 per cent, Then wide variations are in themselves sufficient to suggest the importance of more extended investigations to connect the phosphorus with other factors in individual cases.

Nitrogen Content.—The determination of the nitrogen by the Kjeldahl method presents no difficulties but the value of the determination is somewhat uncertain, in view of the loss of nitrogen which always occurs in the separation of the fat. In different series of experiments we have attempted the extraction of the fat in various ways, and each method seemed to be attended with a marked loss of nitrogen. If the feces are evaporated rapidly on the water-bath and extracted a product is obtained which is sometimes low in nitrogen; this is especially the case if the water-bath evaporation is followed by further drying in the air oven. A decomposition of the original nitrogen complex evidently takes place here.

On the other hand, the extraction of the original moist feces with boiling alcohol gives equally unsatisfactory results, as will be pointed out below. Boiling with alcohol produces a great change in the ratio of phosphorus to nitrogen. To secure a proper nitrogen value we believe the complete, but slow drying is necessary, followed by ether extraction, and this scheme we returned to after trying several others. From the fat sample A secured in this manner we obtained 4.16 mg. of nitrogen for each g. of fat, or nearly 0.42 per cent. From sample B, which was low in phosphorus, we obtained 2.82 mg. of nitrogen for each g. of fat, or 0.28 per cent. As compared with the phosphorus in the same sample this nitrogen is relatively high, and no simple relations appear to obtain in the two cases.

Iodine Number.—The iodine absorption of the crude part is relatively low. In fat A we found the value to be 22.2 per cent., while in fat B it was 24.2 per cent. These are about the values which are found in butter fat and are smaller than those for lard or tallow.

Saponification Number, or milligrams of KOH required for 1 gm. of the crude fat. This test was carried out in the usual manner with an alcoholic solution of potassium hydroxide and gave for fat A a value of 216.7 and for B 153.6. For the ordinary fats the second value is low,

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but for such a mixture as might be here expected it is not abnormal. The crude feces fat always contains cholesterol, which does not saponify, besides other bodies of high molecular weight. The amount of cholesterol in the crude fat may run as high as fifteen per cent. or more, and would produce a marked decrease in the saponification value. For lecithins, on the other hand, the value is relatively high. From a good product made in this laboratory from eggs we found the number 335. For lard and tallow the value is about 200, and for butter fat about 225, in the mean.

A part of this alkali absorption is due to the presence of free fatty or similar acids. In an independent experiment with fat A it was found that 1 g. of the fat dissolved in alcohol required for neutralization 53 mg. of potassium hydroxide, as measured by phenolphthalein.

Experiments with the Acetone Precipitate.

Many methods have been proposed for the recognition of the lecithin-like bodies in fatty mixtures, and as applied to the feces they have frequently given such poor results as to lead to the impression that the lecithin content must be *nil* or very low. As lecithin combines with certain metallic salts readily, attempts have been made to precipitate it quantitatively from mixtures by such substances as cadmium chloride. Some years ago the details of a process for the separation from the yolk of eggs was described by Bergell[1] in which he extracted with alcohol, precipitated with cadmium chloride and recovered the lecithin from the precipitate by decomposition with ammonium carbonate. The results obtained from this process, even where applied to eggs, are far less satisfactory than would appear from Bergell's paper, and several attempts to duplicate his results gave always much lower figures. When applied to our feces fat extraction the results were always uncertain and irregular. The separation was abandoned as not suited to the purpose.

Much depends also on the orignal extraction method employed, and to illustrate the difficulties the following experiments may be cited. About 300 g. of feces was boiled under a reflux condenser with a considerable excess of absolute alcohol, enough to make the mixture contain about 85 per cent. alcohol. At the end of some hours the solution was filtered hot and the filtrate slowly evaporated to dryness. The fatty residue was taken up with chloroform, and the new solution filtered from a small insoluble portion. On adding an excess of acetone to the clear chloroform solution a precipitate was formed which was collected and tested for phosphorus and nitrogen, with these results:

$$P = 0.16 \text{ per cent.}$$
$$N = 3.96 \text{ per cent.}$$

The acetone-chloroform solution was evaporated and the fatty residue treated in the same manner, giving:

[1] Ber., 33, 2584.

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P = 0.04 per cent.
N = 0.77 per cent.

These numbers have little meaning and certainly do not point to a lecithin content in the original feces. The prolonged boilings evidently effect a decomposition of phosphorus and nitrogen compounds. Somewhat similar results were obtained from a second extraction carried out with partially dried feces in the same manner from which it appears that the method is not satisfactory for the purpose, although it has been frequently employed in the search for lecithins as occurring in feces[1]. Some of the negative results reported in the literature are possibly due to this fact.

Our best results were secured by the acetone precipitation of the purified ether extract of fat A described above. A portion of this fatty mass was dissolved in ether and precipitated in a beaker by addition of a very considerable excess of acetone. The precipitate which formed consisted of two parts; the larger portion separated as a sticky, gummy mass which clung to the sides of the beaker after vigorous stirring, while a small amount of a yellowish white granular substance settled out also. This latter could be easily brought into suspension, and by washing with acetone by decantation was almost completely separated. It made up about 1.6 per cent. by weight of the original fat and showed a melting point of 150°. On analysis it gave:

P = 4.14 per cent.
N = 1.27 per cent.

This substance redissolves easily in ether, chloroform and alcohol and on ignition leaves but a trace of ash. The small amount of substance available rendered other tests impossible, but it evidently belongs to the phosphatide group and represents a product higher in phophorus and lower in nitrogen than the typical lecithins. The numbers correspond almost exactly to the ratio:

P : N :: 3 : 2

It should be added that the same product was found in several later extractions, in small amount.

The larger part of the acetone precipitate made up about 35 per cent. of the weight of the purified ether extract as crude fat, and was used for a number of tests. It exhibited, after being washed with acetone and dried over sulphuric acid, the general appearance and behavior of the lecithin bodies and their action toward water.

Melting Point.— As in the case of the original fat this could not be accurately determined, but appeared to be slightly above the boiling point of water. In the capillary tube test the substance softened at the

[1] See Hoppe-Seyler, Chemische Analyse für Aerzte, 6th ed. p. 480.

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boiling temperature, without actually melting. On heating to a higher temperature the mass gradually darkens and chars.

Phosphorus Content.—This was found in the usual manner by the Pemberton method of titration, after fusion with potassium nitrate and sodium carbonate. The titration gave 2.39 per cent. in sample A, which is too low for a real lecithin, undoubtedly, however, the acetone carries down various other products, which are free from phosphorus.

Nitrogen Content.—Some of the washed and dried acetone precipitate was subjected to the Kjeldahl distillation. The ammonia obtained, when reduced corresponded to 0.57 per cent. of nitrogen, which appears very low. It was found, however, that the ether-acetone filtrate from the precipitate was free from more than minute traces of phosphorus and contained considerable nitrogen. The recovered fat gave 0.31 per cent. of the latter element. This may have come originally from other substances than that containing the phosphorus, or it may have been split off, on the other hand, from the phosphorus containing complex during the treatment to which the fat was subjected. If then, assuming this point of view, the whole of the nitrogen could have been secured in the acetone precipitate along with the phosphorus, the nitrogen content would amount to about 1.13 per cent. This accounts fairly well for the whole nitrogen content, and in the acetone precipitate gives a ratio:

$$P : N :: 31 : 14.7, \text{ or } 1 : 1 \text{ atom.}$$

While these percentage numbers are low to indicate a true lecithin as making up the whole of the acetone precipitate, they certainly suggest that such a body may be present in relatively large amounts.

Saponification Number.—This was not found in the acetone precipitate, but was determined in the fat from the ether-acetone solution which was evaporated. The value found was 114.5 while that of the original fat was 216.7. It is evident, therefore, that a body of high alkali-combining power was removed in the acetone precipitation. To account for the low value from the ether-acetone residue this precipitated fraction would have to possess a value of 350 or over. Such numbers are found in the lecithins. The theoretical value for distearyl lecithin is 347. For some egg lecithin prepared in the laboratory we found 335 and for a commercial product containing some moisture and non-saponifiable matter a value of 231, equivalent to over 300 in purified condition. The phosphate group in this combination seems to be wholly indicated by phenolphthalein and in the calculation, therefore, five molecules of alkali were taken for one of the lecithin.

Iodine Number.—This could not be found directly for want of material, but from the value determined with the residue from the ether-acetone

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solution it is evident that this factor is low. In both samples A and B, the fat recovered from the filtrate after precipitation with acetone showed a much higher iodine absorption than was found in the original fat and this can be the case only when the precipitated fraction possesses a low absorbing value.

Taking all these experiments as a whole they undoubtedly point to the pressence of a lecithin-like body in the crude extracted fat. As to the possible origin of this there may be several opinions. The conclusion of Bokay, cited above, that the feces fat contains no lecithin, is based apparently on a few direct feces tests, but largely on the results of some artificial digestion experiments in which he found that lecithin, while slowly attacked by pepsin and acid, is very quickly decomposed by pancreatic extracts, and therefore cannot pass down the intestinal tract as such. This argument probably holds true as far as the larger part of the food lecithin is concerned, but there is every reason to believe that a fraction, and perhaps a large fraction of that found in the feces does not come from the food but from the bile, as a product of the constant breaking down of cells of the liver. This may be discharged at a time and under such conditions that it is not readily attacked by the pancreatic ferment thrown into the intestine. The Bokay view is frequently quoted and is doubtless responsible for some of the misconceptions which obtain on the subject.

In our former paper[1] we called attention to the work of Hammarsten on the bile of different animals, where a high lecithin content is usually found. This fact has one important bearing on our discussion, and it is likely that we should, therefore regard the "phosphatide" or "lecithin" bodies of the feces as excretory products, rather than as waste or unabsorbed material from the food. In pathological conditions the food fat with its small lecithin content may find its way in part into the feces, but in health it is possible that the other source suggested is the more important.

Since the experiments described above were made an article by Erlandsen[2] has come to hand in which methods of extracting the lecithin bodies from certain tissues are very fully described. The author points out, as we have found, that the Bergell method of extraction and precipitation of lecithin gives unsatisfactory results. He finds, also, that acetone carries down nearly the whole of the phosphorus bodies from the ether extract, but holds the separation is not exact enough to be considered accurately quantitative.

NORTHWESTERN UNIVERSITY, CHICAGO,
May, 1907.

[1] loc. cit.

[2] Z. physiol. Chem., 51, 71.

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[CONTRIBUTION FROM THE COMMITTEE ON UNIFORMITY IN TECHNICAL ANALYSIS. IV.]

REPORT OF THE SUB-COMMITTEE ON SHELLAC ANALYSIS.

By PARKER C. MCILHINEY, A. C. LANGMUIR, MAXIMILIAN TOCH, MAX WALLERSTEIN, AUGUSTUS H. GILL.

Received May 31, 1907.

We have considered all the processes that have so far come to our notice having for their object the determination of rosin in mixtures of shellac with rosin, and find that several of the methods depending upon the different powers of shellac and of rosin to unite with the halogens are capable of being used to determine the proportions of rosin and shellac in their mixtures.

We have not found any of the methods in which use is made of the other properties of these two substances, such as solubility, the acidity, or the Köttstorfer figure, sufficiently reliable for general use.

As the absorption of halogen by both shellac and rosin is largely and perhaps entirely by substitution, and not as in the case of fats, by addition, and as the amount of halogen which so replaces hydrogen in the rosin is dependent upon the length of time that the reagent is allowed to act upon it, and also upon such other variables as the excess of the reagent, the temperature, and the relation of the volume of solution to the amount of substance treated, we have considered each of these halogen-absorption processes in the light of its adaptability to the maintenance of standard and uniform arbitrary conditions which will permit results obtained at one time being compared with those obtained at any other time.

The result of our work convinces us that the Wijs process[1] used as proposed by Dr. Langmuir, one of our number, possesses the desirable features of regularity and reliability in a greater degree than any other process which has come to our notice. It is possible by it to carry out a test of a sample of shellac in a couple of hours, and as shellac is a rather expensive material and one very liable to sudden changes in price, it is almost essential that the standard method of testing it should be a rapid one. The Hübl method is deficient in this respect, requiring usually 24 hours to carry out an analysis by it.

The method which we would recommend as a standard one for the determination of rosin in shellac is substantially the one described in Dr. Langmuir's paper in the J. Soc. Chem. Ind., **24**, 12. The solutions required are one of iodine monochloride containing 13 g. of iodine per liter, in glacial acetic acid that has a melting point of 14.7° to 15° C. and is free from reducing impurities, and another of sodium thiosulphate made by dissolving 24.83 g. of the pure salt in a liter of water. In addition to these solutions there is required a quantity of acetic acid of the same strength

[1]Ber., 31, 750, and J. Soc. Chem. Ind., 17, 609.

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as that used for making the solution of iodine monochloride. Pure chloroform and starch are also necessary. The preparation of the iodine monochloride solution presents no great difficulty, but it must be done with care and accuracy in order to obtain satisfactory results. There must be in the solution no sensible excess either of iodine or more particularly of chlorine, over that required to form the monochloride. This condition is most satisfactorily attained by dissolving in the whole of the acetic acid to be used the requisite quantity of iodine, using a gentle heat to assist the solution, if it is found necessary, setting aside a small portion of this solution, while pure and dry chlorine is passed into the remainder until the halogen content of the whole solution is doubled. Ordinarily it will be found that by passing the chlorine into the main part of the solution until the characteristic color of free iodine has just been discharged there will be a slight excess of chlorine which is corrected by the addition of the requisite amount of the unchlorinated portion until all free chlorine has been destroyed. A slight excess of iodine does little or no harm, but excess of chlorine must be avoided.

Introduce 0.200 g. of ground shellac into a 250 cc. dry bottle of clear glass with a ground glass stopper, add 20 cc. of glacial acetic acid and warm the mixture gently until solution is complete (except for the wax). A pure shellac is rather difficultly soluble. Solution is quicker according to the proportion of rosin present; 10 cc. of chloroform are added and the solution is cooled to 21° to 24°. The temperature should be held well within these limits during the test. 20 cc. of Wijs solution are added from a pipette, having a rather small delivery aperture. The bottle is closed and stood in a dark place, and the time noted. It is convenient to keep the bottles during the test partly immersed in water which should be kept as nearly as possible between 22° and 23°.

Pure shellac will scarcely alter the color of the Wijs solution. If in small amount, rosin will produce a slowly appearing red-brown color. In large amount, rosin causes an immediate coloration, increasing in intensity as time passes. After one hour, 10 cc. of 10 per cent. potassium iodide solution are added. The solution is immediately titrated with the sodium thiosulphate solution; 25 cc. or 30 cc. may be run in immediately, unless the shellac is very impure, and the remainder gradually with vigorous shaking. Just before the end, a little starch solution is added. The end point is sharp, as the reaction products of shellac remain dissolved in the chloroform; any color returning after a half minute or so is disregarded.

A blank determination should be run with 20 cc. of Wijs solution, 20 cc. of acetic acid, 10 cc. of chloroform, and 10 cc. of 10 per cent. potassium iodide solution. The blank is necessary on account of the well

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known effect of temperature changes on the volume, and possible loss of strength of the Wijs solution.

In the case of grossly adulterated samples or in the testing of pure rosin, it is necessary to use, instead of the 0.2 g. of material, a smaller amount, say 0.15 g. or even 0.1 g., in order that the excess of iodine monochloride may not be too greatly reduced, as the excess of halogen is one of the factors in determining the amount of absorption. It is safe to say that in case less than 25 cc. of thiosulphate solution are required, another test should be made, using a smaller amount of the shellac to be tested.

In weighing shellac, some difficulty is at times experienced on account of its electrical properties; in very dry weather it may be found that the necessary handling to prepare it for weighing has electrified it and that it may be necessary to leave it on the balance pan at rest for a few minutes before taking the final weight.

In any halogen absorption process it is essential that the substance to be examined should be thoroughly dissolved in a reasonable volume of solvent that is cheap and easily obtainable. In this case glacial acetic acid forms an admirable solvent; the only other solvents which are at all comparable with it are the alcohols, which are too readily attacked by halogens to be used with perfect safety.

The two defects which we have found in glacial acetic acid as a solvent are, first, that it solidifies at a temperature but little below that of the ordinary room, and, second, that the results obtained are to a certain extent dependent upon the strength of the acid used. On account of the first mentioned property it may happen that different lots of glacial acetic acid or of Wijs solution may not be of uniform composition throughout the bottle on account of having been frozen and remelted; this difficulty can easily be obviated by remembering to shake the bottles of acid and of Wijs solution before using the contents; to a neglect of this precaution we are disposed to attribute irregular results which we have sometimes obtained during cold weather.

The second difficulty is entirely obviated by using at all times acid of the same standard strength. Three prominent methods by which the strength of the acetic acid might be determined, namely, titration with alkali, the determination of specific gravity, and the determination of the melting point, we have investigated as to their suitability for use in this connection. Of the three we greatly prefer the melting point determination, both on the score of accuracy and of speed. Titration we find least accurate of all, and such accurate determinations of specific gravity as would be necessary in making use of it as a criterion of purity would require an almost prohibitive amount of time and attention. Furthermore, the ultimate standard of a melting point determination, an accurate ther-

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mometer, is a much more satisfactory one and one more easily duplicated than is the case in the other two methods.

We have, therefore, in the description of the method, specified rather the melting point of the acid to be used than its strength as expressed by percentage.

The method which we have used is a simple and rapid one, being in fact the "titre" method in common use for determining the melting point of fatty acids generally. An 8-inch test tube is about half filled with the acid to be tested, the contents chilled rapidly to about 10° or 11° and a delicate and accurate thermometer, graduated at least to tenths of a degree, suspended in the acid in the test tube, the latter being placed in a wider test tube closed by a cork through which the test tube containing the acid is inserted; the whole arrangement is chilled by being immersed in ice water; the acetic acid in a few minutes begins to crystallize, and the temperature of the supercooled acid rises to its true melting point, where it remains stationary for some time. In the case of acetic acid of such strength as is used in the process this simple procedure gives the required information in a few minutes; with weaker acetic acid greater care is necessary to insure accuracy. The acid in the test tube should not have begun to crystallize until some minutes after it has been chilled in cold water and mounted in a larger tube; if it does begin to crystallize too soon, that is, before the cooled acid has had sufficient time to become of uniform temperature throughout, the acid should be well stirred with the thermometer before the crystallizing process has gone very far.

The melting point of acetic acid containing various percentages of water has been determined by Rudorff,[1] as follows:

Per cent. of real acetic acid.	Melting point.
100.	16.75° C.
99.5	15.65° C.
99.	14.80° C.
97.09	11.95° C.
95.24	9.40° C.

In Thorpe's Dictionary of Applied Chemistry and also in Rudorff's paper in the Pharmaceutical Journal and Transactions the melting point given for acid of 99.5 per cent. strength is 16.65°, but this appears to have been a misprint.

A great deal of work had been done with this process before it was understood that the strength of the acid had any serious effect upon the results; numerous lots of acid had been obtained and used which as the event proved must all have been of approximately the same strength; by

[1] Berichte, 3, 390, and Pharmaceutical Journal and Transactions, [3] 2, 241. See also Beilstein, 3d Ed., 1, 399-400.

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comparing the results previously obtained upon standard samples of shellac, using acid of untested strength, with those later obtained with acids of known melting point, it appears that the mass of valuable data which had been obtained, largely by Dr. Langmuir, concerning the iodine figures of pure shellac had been obtained with acid having a melting point of approximately 14.8°. We have, therefore, adopted as the standard strength of the acid used in this process the strength which corresponds to a melting point of 14.7° to 15°.

In order to ascertain quantitatively what are the effects of using acids of different strength, we have made several series of experiments in which the strength of the acid was the only variable. One such series was made upon a lot of shellac which had previously been tested a great many times and had always given a figure of approximately 17.7°. A quantity of Wijs solution was prepared, using acid having a melting point of 14.95°, and with this Wijs solution three tests were made upon the same shellac, using in each test for dissolving the shellac acetic acid of different strength; acid of 11.80° M. P. gave an iodine figure of 14.67, acid of 14.95° M. P. (the same as that used for the preparation of the Wijs solution) gave an iodine figure of 17.59, while acid of 16.40° M. P. gave an iodine figure of 20.48.

We have satisfied ourselves that equally correct determinations of the proportion of shellac and rosin in a mixture can be made by the Hübl, the Hanus, the Wijs and the bromine methods, providing that in each case pains are taken to examine a considerable number of pure shellacs and of rosins to form a satisfactory basis of calculation.

Of these methods the bromine method is the simplest, as the standard solution is very simply made by adding a given volume of bromine to a given volume of glacial acetic acid.

The Hanus solution comes next in simplicity, but we are of the opinion that if sufficient care be taken in the preparation of the iodine bromide solution to insure the exact relation of iodine and bromine to each other that is necessary, there is little to choose in this respect between the Hanus and Wijs methods.

The reliability of any of these methods depends largely upon the number of determinations which have been made by it upon samples of shellac and of rosin which are known to be pure. In this respect we believe the Wijs method to be very decidedly preferable, on account of the number of data obtained by Dr. Langmuir by this method, and using the particular conditions advocated in his paper already referred to. We have carefully considered the merits of each of these conditions, the weight, volume, time, and temperature, and are of the opinion that they can not for general use be modified with advantage.

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Unbleached shellac, when examined by this process, shows an iodine absorption varying from 15 to 18 per cent.

No pure shellacs show a higher percentage than 18. As shellac is relatively a high priced material and as the variation between its highest and lowest figure is not great, we believe that 18 should be taken as the standard figure for shellac determined by the method which we have described.

In the case of rosin the variation between the highest and the lowest figures is much greater; different grades of rosin give figures which vary from about 175 in the darkest varieties to about 260 in the very lightest colored or W.W. grade. Of course, theoretically, any grade of rosin might be mixed with shellac, but the grades that are actually used in shellac adulteration seem to be intermediate ones, having probable iodine figures, as determined by this method, between 200 and 225.

As it is an accepted principle that a standard method should be so devised that its inaccuracies shall work in the direction of favoring the seller rather than of condemning too severely the article sold, we approve the rather high value taken by Dr. Langmuir for rosin, 228, although if the shellac is dark in color the rosin used to adulterate it may also be dark and have a somewhat lower iodine figure. The results of using in this method the figure 18 as the iodine figure of shellac and 228 as the figure for rosin may be, under some circumstances, that a slightly lower percentage of rosin will be found than that actually present.

If y = per cent. rosin
M = iodine number of shellac
N = " " " rosin
A = " " " mixture

$$\text{Then } y = 100\frac{(A - M)}{N - M}$$

In order to test practically the degree of accuracy and of regularity to be expected from the method, we caused to be prepared by Dr. Langmuir three samples of artificial mixtures of shellac and rosin, designated respectively as "A," containing 5 per cent. of rosin; "B," containing 9 per cent., and "C," containing 13.5 per cent. These samples were distributed to the members of the committee and analyzed, the true composition remaining unknown to those making the test until the work had been completed. Two members analyzed the samples by the method here recommended and two others by the Hübl method. The results were as follows:

Analyst.	Method	Sample "A" per cent. rosin.	Sample "B" per cent. rosin.	Sample "C" per cent. rosin.
1	Committee	3.3	7.8	12.2
1	Hübl	3.15	7.65	13.27
2	Committee	3.2	7.15	11.6
3	Hübl	4.3	7.5	12.2

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The use of the figure 200 instead of 228 as the iodine figure of rosin by this method will result in giving the true percentage of rosin with a little greater accuracy in most cases; we believe, however, that in order to guard against the rather remote possibility that the use of the figure 200 might give a percentage of rosin slightly too high, it is better policy to use the figure 228.

THE ACTION OF BARIUM PEROXIDE AND HYDROGEN PEROXIDE UPON FORMALDEHYDE.

By C. ALLAN LYFORD.

Received June 13, 1907.

The problem of the action of peroxides upon solutions of formaldehyde has been left in a rather unsettled condition. The present research has for its purpose the clearing up of this question. While experimenting upon the oxidation of formaldehyde it was believed that by using barium peroxide there might result mutual oxidation and reduction with the production of barium formate. Upon looking up the literature of the subject the writer found that Geisow[1] believes to have obtained only barium carbonate and hydrogen from the interaction of these two substances. He says he was unable to detect formic acid as an intermediate product either in neutral or acid solution. Geisow gives the following reaction:

$$HCHO + BaO_2 = BaCO_3 + H_2.$$

So far as the writer can ascertain, this work has neither been confirmed nor disproved by other writers.

For a number of reasons this reaction does not seem probable. In the first place, acetaldehyde forms a hard resin with barium peroxide, no methane being evolved. If there were such an easy direct removal of the carbonyl group one would not expect a resin to be formed. Geisow states that the dioxides of lead and manganese acting upon formaldehyde in neutral solution produce formates and hydrogen. It is known that uranium peroxide acting upon formaldehyde in neutral solution produces uranyl formate and hydrogen.

$$PbO_2 + 2HCHO = (HCOO)_2\,Pb + H_2.$$

$$UO_4 + 2HCHO = (HCOO)_2\,UO_2 + H_2.$$

In alkaline solutions it has been shown that hydrogen peroxide acts upon formaldehyde according to the following equation[2]:

$$2HCHO + 2NaOH + H_2O_2 = 2HCOONa + H_2 + 2H_2O,$$

(in cold), from which it would follow that the reaction with sodium peroxide and sufficiently dilute formaldehyde would be:

$$2HCHO + Na_2O_2 = 2HCOONa + H_2.$$

If 30 per cent. formalin be dropped upon sodium peroxide, there is,

[1] Geisow, Ber., 37, 515.

[2] Blank and Finkenbeiner, Ber., 31, 2979.

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evidently, a reduction to metallic sodium with explosive violence, and the sodium then burns with the characteristic flame.

$$2HCHO + Na_2O_2 = Na_2 + 2CO_2 + 2H_2.$$

It is seen that in alkaline solution formic acid after being produced, is fixed by the excess of base, and is apparently not further attacked in the primary reaction. It should follow that if barium peroxide were used the reaction should be approximately as follows:

$$2HCHO + BaO_2 = (HCOO)_2 Ba + H_2.$$

This does not agree with Geisow's statement of the case. In acid solutions peroxides invariably give carbon dioxide and hydrogen, or water as oxidation products.

Since, strictly speaking, it is impossible to work with barium peroxide in neutral solutions, because of its slow decomposition, even in cold water, the case reduces itself to the action of a peroxide upon formaldehyde in alkaline solution. The only way it seems possible that carbon dioxide can result is by using free acid, which of course would change the case to that of the action of a peroxide in acid solution. The fact that the writer finds barium formate is produced by the action of barium peroxide upon formaldehyde makes it certain that the reaction is not so simple as Geisow believes it to be. The writer cannot see how Geisow obtained hydrogen to the extent of 98.15 per cent. of the theoretical amount demanded by the equation:

$$HCHO + BaO_2 = BaCO_3 + H_2.$$

There is at the most only a very small amount of barium carbonate produced, and that seems to be chiefly due to the action of atmospheric carbon dioxide upon the mixture. Any evidence as to a difference between barium peroxide as a true "peroxide" and manganese dioxide as a true "dioxide," which Geisow seeks to bring forward is unsound, as it is based upon evidently false results. Barium peroxide produces formate just as do the dioxides of lead and manganese, and so far as its action upon formaldehyde is concerned, may possess a structure identical with that of manganese dioxide.

In the experimental work the writer has used pure barium peroxide prepared from hydrogen peroxide and recrystallized barium hydroxide. The formaldehyde was in some cases prepared from paraformaldehyde, and was in others the best commercial formalin carefully standardized by the Haywood-Smith modification of the Blank-Finkenbeiner method[1].

The strength of aldehyde is given in per cent. by volume.

EXPERIMENTAL PART.

A few cubic centimeters of 35 per cent. formaldehyde were put upon a large mass of barium peroxide and allowed to act. The peroxide was in excess. The hard cake finally produced after violent effervescence, was

[1] Haywood-Smith, This Journal, 27, 1183.

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taken up with water and nearly all went in solution. The solution was treated with carbon dioxide, boiled, filtered, and evaporated to a small volume. A few drops of silver nitrate solution then produced a white crystalline precipitate of silver formate which soon turned dark in the light, depositing black, amorphous silver. This is characteristic of silver formate.

20 g. of barium peroxide were treated gradually with 40 cc. of neutral 35 per cent. formaldehyde. After the action had ceased there was an excess of aldehyde. The mixture was allowed to stand half an hour with occasional shaking, so as to use up all the peroxide. Water was added, and nearly all the original mass went into solution. The solution was alkaline, owing to the reduction of some peroxide to barium oxide by the action of water and the nascent hydrogen evolved. The barium hydroxide was removed by treating the hot solution with carbon dioxide and filtering. Upon evaporation, over 20 g. of barium formate were recovered in excellent white crystals, with a very slight odor of formaldehyde, which was removed by again dissolving and evaporating down with frequent additions of alcohol.

Barium Formate and Hydrogen produced.—10.88 gr. barium peroxide and 30 cc. water were treated in a flask with gradual additions, during three minutes, of 30 cc. of 35 per cent. formaldehyde solution (excess). The temperature was kept at 20°-25° by cooling in water. 1202 cc. (reduced) of hydrogen, corresponding to 0.1077 g., were collected. From the solution after filtering off a very small precipitate of barium carbonate, little carbonate could be thrown down with carbon dioxide, showing that not much reduction by the action of water and of hydrogen had taken place. 14.3 g. barium formate were recovered from the solution. The salt was perfectly crystalline. Analysis showed it to be nearly pure barium formate (Ba = 60.1 per cent.). Solutions of the salt gave the characteristic test with silver nitrate solution; also, treated with dilute sulphuric acid and warmed, it gave a strong odor of formic acid.

By Geisow's reaction, $HCHO + BaO_2 = BaCO_3 + H_2$, or by the following one, $2HCHO + BaO_2 = (HCOO)_2 Ba + H_2$, 10.88 g. barium peroxide would set free about 0.1284 g. of hydrogen. It is evident that about 200 cc. of the gas disappeared in some way. This may be due either to oxidation of some hydrogen while in the nascent condition, or to other reactions taking place which do not liberate hydrogen. However, the rough agreement of the yields 14.3 g. barium formate and 0.1077 g. hydrogen with the theoretical figures 14.6 g. and 0.1284 g. respectively, makes it certain that the greater portion of the reaction takes the form of

$$2HCHO + BaO_2 = (HCOO)_2 Ba + H_2,$$

and that under the conditions, only a small amount of barium is converted into any other form than formate. The amounts of formate and

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hydrogen obtained are respectively 97.9 and 83.9 per cent. of the theoretical demanded by the above equation, while Geisow's equation demands twice as much hydrogen.

3.017 g. barium peroxide were treated with 10 cc. of water, and a slight excess of 20 per cent. formaldehyde. 3.7262 g. of formate were obtained by direct weighing of the crystals left upon evaporating the mother liquor after removing all other barium. Here 91.97 per cent. of the barium was changed to formate.

2.3582 g. barium peroxide and 10 cc. of water were treated with a slight excess of 3.78 per cent. (volume) formaldehyde. After removing all barium other than formate, there were obtained from the solution 2.9417 g. barium sulphate. Here 90.7 per cent. of the barium was converted to formate in the reaction with the aldehyde. It is evident that barium formate is produced either with dilute or strong formaldehyde.

Since in one of the earlier experiments it was evident that there was considerable loss of hydrogen, it was attempted to see if by altering the conditions a more quantitative yield might be obtained. Occasion was also taken to study the effect of time upon the reaction.

Ten g. barium formate, and 25 cc. water were treated with 5 cc. 37.8 per cent. formaldehyde (not excess). The aldehyde was added instantaneously. Most of the gas came off in two minutes. The temperature was kept down by cooling with a water-bath. 593 cc. (reduced) of hydrogen were collected. The reading was taken after a quarter of an hour.

The above experiment was repeated except that the aldehyde was added slowly, in small amounts during one-half hour. The gas was evolved very gradually during three-quarters of an hour. One hour after the beginning of the experiment the reading was taken. 601 cc. (reduced) of hydrogen were collected.

According to the experiments no appreciable quantity of hydrogen which would be evolved upon instantaneous action, is fixed as water during prolonged action. The insolubility of the peroxide would not allow of much reduction in one hour at low temperatures. The increased volume of gas actually obtained in the second experiment is doubtless due to the increased time the peroxide was in contact with the water, thus liberating some oxygen. The amount of oxygen was so small, however, that it could not be directly measured with certainty, though there was a slight contraction with pyrogallic acid, using a 30 cc. fraction of the gas.

It is evident that the deficiency of hydrogen below the theoretical is due, not so much to the fixing of some hydrogen as water, as to reactions not producing hydrogen taking place along with the primary reaction. Possibly the following takes place:

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$$2HCHO + 2BaO_2 = (HCOO)_2Ba + Ba(OH)_2.$$

601 cc. of hydrogen is equivalent to 0.5385 g., which is 85.4 per cent. of that which would theoretically be generated from the amount of aldehyde used according to the reaction,

$$2HCHO + BaO_2 = (HCOO)_2Ba + H_2,$$

and only 42.7 per cent. of the amount demanded by Geisow's reaction.

By the use of more dilute formaldehyde solution, more quantitative yields of hydrogen result.

Two g. barium peroxide and 10 cc. water were treated in a special apparatus with an instantaneous addition of 5 cc. of 3.78 per cent. formaldehyde solution, and the mixture shaken from time to time. At intervals, readings of the gas evolved were taken as shown in the table. For the reaction,

$$2HCHO + BaO_2 = (HCOO)_2Ba + H_2,$$

there were taken the equivalent of 0.0063 g. of hydrogen.

Time.	Vol. H_2.	Grams H_2.	Available H_2.	Per cent. evolved.
10 min.	67.8 cc.	0.00607	0.0063 gr.	96.4
20 min.	68.0 "	0.00609	"	96.7
1 hr.	69.0 "	0.00618	"	98.1
1½ hrs.	69.8 "	0.00625	"	99.2
2 hrs.	70.5 "	0.00632	"	100.2
15 hrs.	75.3 "	0.00675	"	107.1
24 hrs.	77.3 "	0.00693	"	109.9

Under the conditions employed it is seen that in from 1½ to 2 hours, a fairly accurate estimation of the formaldehyde may be made from the volume of hydrogen liberated. Geisow claims, however, that from a solution of 3.7 per cent. by weight he obtained 27.8 cc. of hydrogen per cc. of the aldehyde solution. Taking the above two hour determination as closely approaching the theoretical for the reaction producing barium formate, it is seen that for one cubic centimeter 14.1 cc. of gas result. The solution worked with, being 3.53 per cent. by weight, is closely comparable to Geisow's 3.7 per cent. solution. Geisow gets, or claims to get, twice as much gas as seems possible to obtain. Other experiments have never failed to give only half as much gas as was to be expected from Geisow's reaction. Geisow's hydrogen may have contained appreciable amounts of oxygen, derived from the slow decomposition of the peroxide with water.

The Action of Hydrogen Peroxide upon Formaldehyde.— Because of Geisow's conclusions as to the action of hydrogen peroxide upon formaldehyde it was somewhat surprising to find that much free formic acid can be detected. This suggested that his idea of the mechanism of the reaction is not correct. His equation to show the reaction is $HCHO + H_2O_2 = H_2O + CO_2 + H_2$, no formic acid being produced in any stage of the reaction. It will be shown that this cannot satisfy the requirements.

Five cc. of a 37.8 per cent. formaldehyde solution were treated with

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50 cc. 3 per cent. hydrogen peroxide of neutral reaction. The solution was warmed fifteen minutes under a reflux condenser. After all effervescence had ceased the temperature was allowed to rise to the boiling point for fifteen minutes longer. At the end of this time all odor of formaldehyde was gone, and the odor of formic acid was very strong in the hot solution, which was also of a strong sour taste. The solution was then titrated against 0.525 normal solution of sodium hydroxide, with phenolphthalein.

85.7 cc. sodium hydroxide were required, or 2.0696 g. formic acid were present in the solution. Five cc. of 37.8 per cent. formaldehyde would give 2.89 g. of acid. 71.6 per cent. of the aldehyde was changed to acid. Only a small portion of the gas evolved from this reaction was carbon dioxide, for very little precipitate was given with barium hydroxide when the gas was passed through it. Later, carbon dioxide appeared to come off in greater abundance.

Formaldehyde Changed to Formic Acid by 3 Per cent. Hydrogen Peroxide.—5 cc. of 37.8 per cent. formaldehyde and 50 cc. of 3 per cent. hydrogen peroxide (10 cc. at a time) were boiled under a reflux condenser until no odor of aldehyde was detected. The free acid was then neutralized with sodium hydroxide. 3.4 g. of sodium formate were recovered. This is equivalent to 1.5 grams of aldehyde. 1.89 g. of the aldehyde were taken, consequently 79.36 per cent. of it was oxidized to free acid. That the residue was sodium formate is proven by the fact that the solution gave colorless crystals of silver formate, which quickly decomposed to silver on exposure to light. Also when the residue was heated for a time at 300°, and then dissolved in water, barium hydroxide gave a white precipitate of barium oxalate insoluble in excess of dilute hydrochloric acid.

Since formic acid is produced in large quantities by the action of hydrogen peroxide upon formaldehyde, it was thought that this should be borne out by analysis of different fractions of the gas given off. An apparatus was fitted up for collecting the gases in fractions, so that they could be transferred to a Hempel gas burette for analysis.

Five cc. of 3.15 per cent. formaldehyde were treated in the special apparatus with 35 cc. of 3 per cent. hydrogen peroxide solution, the temperature being kept at 80°. The gases were collected in consecutive fractions and analyzed.

Fraction.	Time collecting.	Total cc.	CO_2.	O_2.	H_2.	Per cent. by volume. CO_2.	O_2.	H_2.
1	20 min.	30.0	3.8	9.6	16.6	12.65	31.97	55.38
2	35 "	31.2	11.2	10.5	9.5	35.84	33.60	30.56
3	50 "	24.4	11.2	8.9	4.3	45.81	36.40	17.59
4	1½ hrs.	29.6	14.1	12.5	3.0	47.66	42.25	10.14
5	2¾ "	36.6	11.6	23.8	1.2	31.67	64.97	3.28
6	5 "	35.9	9.5	25.5	0.9	26.41	70.89	2.50
	Totals,	187.7	61.4	90.8	35.5	32.71	48.37	18.91

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After the experiment 25 cc. more hydrogen peroxide were added to the aldehyde, and a subsequent fraction collected inside of one-half hour contained 2.8 cc. of carbon dioxide, showing that the formic acid was still not all oxidized. The increase in the percentage of oxygen in successive fractions is due to the increased time during which the peroxide is undergoing decomposition, while the hydrogen soon falls off, as the aldehyde disappears.

0.1575 g. of the aldehyde should give 0.231 g. carbon dioxide, or 117.2 cc. Only 58 cc. (reduced) were collected, showing that only 50 per cent. of the formic acid had been oxidized. In dilute solutions formic acid is only slowly affected by weak hydrogen peroxide. The sudden stop in the evolution of hydrogen after the fourth fraction shows that the aldehyde had practically all been converted into some other product by that time.

Geisow claims to have obtained a quantitative yield of hydrogen according to the equation :

$$HCHO + H_2O_2 = H_2 + CO_2 + H_2O.$$

In this experiment, using 30 per cent. peroxide and 3.7 per cent. (by weight) aldehyde, he was unable to detect the presence of formic acid. The above equation calls for equal volumes of hydrogen and of carbon dioxide. The fact that the evolution of hydrogen ceases before half the carbon is oxidized, and that the quantity is so small, shows that Geisow's idea of the reaction is incorrect. The experiments bear out the writer's opinion that several reactions are proceeding simultaneously. If formic acid is produced as an intermediate product, the following equations explain well the phenomena observed :

$$2HCHO + H_2O_2 = 2HCOOH + H_2.$$

The above reaction predominating in the first part of the process, is later followed by—

$$2HCOOH + 2H_2O_2 = 2H_2O + 2CO_2 + 2H_2O.$$

Carbon dioxide is evolved only as formic acid is produced and oxidized, not immediately, as by Geisow's reaction. There seems also to be a reaction as follows :

$$HCHO + H_2O_2 = HCOOH + H_2O.$$

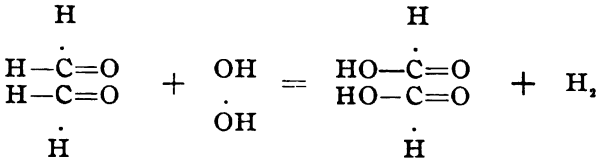
Also it is probable that considerable of the peroxide is reduced by the nascent hydrogen, for the yield of this gas is much too low for the amount of carbon dioxide coming off. The above two principal equations may be combined into an empirical one demanding at least twice as much carbon dioxide as hydrogen.

$$2HCHO + 3H_2O_2 = 2CO_2 + H_2 + 4H_2O.$$

Since formic acid is produced as an intermediate product, the hydrogen

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must come from the aldehyde, half the hydrogen from each of two molecules coming off simultaneously.



Since by the action of 30 per cent. hydrogen peroxide upon dilute formaldehyde, Geisow claims to have obtained a theoretical yield of hydrogen for his equation, it was thought desirable to repeat his experiment as near as his meagre description would allow. First, however, it was desirable to see if strong peroxide would produce any formic acid.

Aldehyde Converted to Formic Acid by 30 per cent. Hydrogen Peroxide.—5 cc. 37.8 per cent. of formaldehyde and 15 cc. of water were treated with 20 cc. of 30 per cent. hydrogen peroxide for fifteen minutes under a reflux condenser at boiling temperature. At the end of this time there was a very strong odor of formic acid and no odor of the aldehyde. Titration with standard alkali showed the presence of 1.7557 g. formic acid. Since the theoretical yield is 2.89 g., it follows that 60.7 per cent. of the aldehyde was changed to acid.

The gases evolved in another experiment with strong peroxide were analyzed in successive fractions. In the experiment it was attempted to adhere to conditions like those described in one of Geisow's experiments.

Five cc. 3.78 per cent. formaldehyde (3.53 per cent. by weight) were added to 15 cc. water, and placed in the apparatus previously used. 20 cc. 30 per cent. hydrogen peroxide were added, and fractions taken as follows, and analyzed. No carbon monoxide was detected.

ANALYSIS OF GAS FRACTIONS.

	Time.	Temperature.	Total cc.	CO_2.	O_2.	H_2.
1	15 min.	70°	55.0	1.8	52.1	1.1
2	15 min.	70°	57.0	3.9	52.1	1.0
3	75 min.	45°	50.9	4.4	45.4	1.1
4	2 hrs.	45°	56.6	5.1	50.5	1.0
5	4 hrs.	40°	58.2	5.3	51.8	1.1
6	5 hrs.	40°	43.6	5.4	36.1	2.1
7	5 hrs.	40°	41.0	6.2	33.0	1.8
8	5 hrs.	40°	51.6	7.8	42.6	1.2
9	15 hrs.	20°	64.6	7.2	53.0	4.4
10	15 hrs.	20°	62.3	7.5	50.8	4.0
11	3 hrs.	45°	68.6	9.6	56.9	2.1
12	4 hrs.	45°	44.4	8.4	35.1	0.9
13	4 hrs.	45°	49.2	7.3	41.4	0.5
14	4 hrs.	45°	45.3	7.0	38.1	0.2
15	4 hrs.	45°	46.8	6.8	40.0	0.0
			795.1	93.7	678.9	22.5

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If the carbon in the 0.189 g. formaldehyde used were completely oxidized to carbon dioxide, there should be 140.6 cc. carbon dioxide. It is evident that in seventy-two hours only a little over one-half the carbon has been oxidized; also the yield of hydrogen is not nearly the theoretical amount for Geisow's reaction. There must be much hydrogen oxidized to water by the oxygen constantly evolved in the spontaneous decomposition of the peroxide always taking place.

Here again, with strong hydrogen peroxide, there are unmistakable proofs of the presence of formic acid. It will be observed that increase in temperature of the reaction decreases the amount of hydrogen collected, owing probably to its more complete oxidation to water. Decrease in temperature increases the time necessary to collect fractions. Analysis of the fractions in this case does not show the two separate stages in the reaction as in the case with dilute hydrogen peroxide. This is due all through to the fact that most of the hydrogen is undoubtedly fixed as water by the strong peroxide employed. The increasing amounts of carbon dioxide, however, indicate greater concentration and greater decomposition of formic acid as the reaction proceeds to a certain stage. As formic acid disappears, the carbon dioxide falls off.

Conclusions.

1. *The Reaction with Barium Peroxide.*—The reaction with barium peroxide proceeds chiefly only as far as the production of barium formate; usually from 90 to 95 per cent. of the barium appearing in that form. The amount of hydrogen probably does not reach such high figures on the average. Though the reaction may be empirically shown by the equation,

$$2HCHO + BaO_2 = (HCOO)_2Ba + H_2,$$

it is most certain that other and intermediate reactions take place. The evolution of hydrogen does not take place until after several seconds have elapsed. After the reaction has taken place, the solution is strongly alkaline to litmus, showing the presence of barium hydroxide. The influence of an alkali upon the oxidation of formaldehyde by a peroxide is always to hasten the process, as happens in the Blank and Finkenbeiner reaction. Also there is some evidence of the presence of small amounts of hydrogen peroxide in the solution. If the above equation solely represents what takes place, there could result no marked quantity of barium hydroxide in the short interval of a couple of minutes, if the temperature is kept at 20° to 25°. The writer feels justified in provisionally explaining the reaction as follows:

First and continually there is a comparatively slow reaction shown by this equation,

$$(1)\ HCHO + BaO_2 + H_2O = HCOOH + Ba(OH)_2.$$

This gives free formic acid, which acts upon any barium monoxide or

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dioxide with which it may come in contact. Coming in contact with peroxide it liberates hydrogen peroxide.

(2) $2HCOOH + BaO_2 = (HCOO)_2Ba + H_2O_2$.

Then reaction (3) liberates hydrogen.

(3) $2HCHO + H_2O_2 = 2HCOOH + H_2$.

Since the reactions take place at the surface of the peroxide, the hydrogen peroxide acts upon the aldehyde in a very concentrated condition, thus causing reactions (2) and (3) to take place much faster than (1). Reactions (2) and (3), alternating and taking place much faster than (1), may be combined in the form of (4).

(4) $2HCHO + BaO_2 = (HCOO)_2Ba + H_2$.

This tells the story of the whole reaction almost quantitatively. However, since reaction (1) undoubtedly takes place to some extent, it is evident that the yield of hydrogen, if accurately separated from any oxygen, can never be quite quantitative.

2. *The Reaction with Hydrogen Peroxide.*—The action of hydrogen peroxide upon formaldehyde is not as simple as it has been credited to be. Formic acid is always produced as an intermediate product, along with hydrogen; then the acid may be oxidized to carbon dioxide and water. If all carbon dioxide and all hydrogen could be collected, the volume of carbon dioxide would be about twice that of the hydrogen. The reaction approaches

$$2HCHO + 3H_2O_2 = 2CO_2 + H_2 + 4H_2O,$$

with the production of formic acid as an intermediate product, according to the following reaction,

$$2HCHO + H_2O_2 = 2HCOOH + H_2.$$

Except upon prolonged action, most of the reaction goes no farther than this intermediate stage.

Since the above work was completed, the writer has found that Kastle and Loevenhart[1] worked upon the basis of the fact that formic acid is produced in the action of hydrogen peroxide upon formaldehyde. They did not realize the character of the reaction, however, for there is no mention made of the production of hydrogen, nor of the subsequent oxidation of formic acid to carbon dioxide, which latter fact must appreciably affect their values for the coefficient of velocity of formation of formic acid from the aldehyde.

CHEMICAL LABORATORY, CLARK UNIVERSITY,
May 15, 1907.

[CONTRIBUTIONS FROM THE BUREAU OF CHEMISTRY. U. S. DEPARTMENT OF AGRICULTURE, BUREAU OF CHEMISTRY, BOSTON LABORATORY.]

FORMIC ACID AS A PRESERVATIVE.[2]

By BERNARD H. SMITH.

Received May 10, 1907.

The antiseptic and preservatory properties of formic acid have recently

[1] Kastle and Loevenhart, This Journal, 21, 262.

[2] Published by permission of the Acting Secretary of Agriculture.

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been referred to in several articles[1], which are of particular interest at this time because of the widespread attention attracted by all matters relating to the purity of foods. Preservatives under trade names are also appearing which contain a formate as their principal antiseptic ingredient. The chemical literature as a whole contains very little concerning the preservative properties of formic acid though it appears that such characteristics have long been recognized[2]. Because of the frequent occurrence of formic acid in nature and of its being an oxidation product of many materials that go to make up foods, complex questions are likely to arise should this substance come into general use as a preservative.

Efficiency as a preservative. Having found a liberal quantity of formic acid in a sample of French cherries, and becoming interested as to the amount required to preserve ordinary perishable food products, some experimental work was undertaken with a view of obtaining additional information as to its relative efficiency as an antiseptic agent, and to determine if possible which of the usual tests would be of the greatest value in detecting formic acid in foods.

In carrying out the former, though other fresh foods were originally included in the tests the work was ultimately confined to stewed tomatoes, it appearing that these when untreated had a tendency to decompose quite uniformly and with rapidity. In interpreting results of this character it is necessary to keep in mind that some preservatives are more efficient for certain food products than for others. This is particularly true of salicylic acid of which considerable quantities are necessary to affect certain putrefactive germs, and the same is true of formic acid though perhaps not in such a marked degree. In all tests blank controls, and samples treated with 1/10 of a per cent. of salicylic acid and benzoic acid were compared with those to which formic acid in varying amounts had been added. Some of the trials were conducted at different temperatures and some with a specific mould in stoppered receptacles, while others were left quite freely exposed to the air, under condition most favorable for decomposition. Though with the latter method samples side by side and treated in the same way may vary somewhat, these results are of perhaps greater value because in them the irregularities of natural conditions are more closely approximated. The following table gives the results of a series of experiments made in this way, which indicate that formic acid is doubtless efficient as a preservative when present in considerable quantities.

[1] Hoffmann. Apoth.-Ztg., 1904, 78. Von Kuttner and Ulrich. Oeffentl. Chem. XII., 201. Lebbin. Chem.-Ztg., 30, 1909.

[2] Jodin. Compt. rend. 96, 1179. Vogel. Sitzungsber. Akad. Wissensch., Munich, 1882, 345.

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MATERIAL,—TOMATOES.

Amount Acid.	Souring or Moulding.
Control (without acid).	Sour after 2 days.
0.1 per cent. Formic (100% sol.)	Mould and sour after 7 days
0.1 " " " " "	" " " " 7 "
0.3 " " " " "	" " " " 12 "
0.3 " " " " "	" " " " 18 "
0.5 " " " " "	" " " " 25 "
0.5 " " " " "	" " " " 34 "
0.7 " " " " "	" " " " 45 "
0.7 " " " " "	Good " 85 "
1.0 " " " " "	" " 85 "
1.0 " " " " "	Mould " 45 "
2.0 " " " " "	Good " 85 "
2.0 " " " " "	" " 85 "
0.1 Benzoic acid	" " 85 "
0.1 " "	" " 85 "
0.1 Salicylic acid	Sour " 9 "
0.1 " "	" " 9 "

As the table tends to show formic acid ranks lower than benzoic or salicylic acids as an antiseptic agent, which has been noticeable in all trials made.

The relatively low efficiency of salicylic acid as compared with benzoic acid in preserving tomatoes was not expected, but data obtained from manufacturers of tomato products who have used both indicates that benzoic acid is generally recognized as superior for this purpose; but the reverse is apparently true with many other foods.

One-tenth of a per cent. of the sodium salt of benzoic acid is usually regarded as satisfactory in preventing fermentation in goods packed commercially, and to produce similar results using formic acid it would probably be necessary to use from three to five tenths of a per cent.

Separation from food products.—Distillation after acidifying with phosphoric acid appears to be the most practical method of separating formic acid from a food material, but the phosphoric acid should be tested to make sure that it is free from volatile acids. The distillation is preferably done with a current of steam by the same method employed in the determination of the volatile acids in a vinegar. In distilling a food product with a current of steam, more particularly concentrated saccharine solutions, care should be taken not to allow the contents of the distilling flask containing the material to be greatly reduced in volume or small quantities of formic acid will be formed by decomposition. As has been pointed out[1], formic acid does not distil as readily as might be supposed, for during the first part of a distillation it comes over comparatively slowly, and in order that the total amount of the formic acid in the sample be recovered it is necessary to continue the distillation until the bulk of the

[1] Duclaux. Ann. chim. phys. (5) 11, 233.

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distillate is from three to five times that of the sample taken. A distillation of a water solution, without the use of a current of steam, continued until ninety per cent. of the liquid had distilled, gave only sixty per cent. of the formic acid added. The distillate will of course contain other volatile acids which are present as well as other volatile substances, such as aldehydes or alcohol. As sulphurous acid and aldehydes are active reducing agents, it is necessary to make sure of their absence before relying upon certain of the reducing tests.

Qualitative tests.—The following are the most important qualitative tests for formic acid as given in the books: Silver nitrate and mercuric chloride are reduced by formic acid or formates of alkali salts, especially in warm solutions. Metallic silver and mercurous chloride are produced. Potassium permanganate is reduced upon which reaction several quantitative methods are based. Ferric chloride or nitrate, when added to a neutral solution of a formate of an alkali metal gives a deep red color. Certain metallic formates are insoluble in alcohol while the corresponding acetates are soluble. Concentrated sulphuric acid evolves carbon monoxide from formic acid or a formate. Sulphuric acid and alcohol when heated with a formate generate ethyl formate, having the odor of peach kernels. Unless a very large quantity of formic acid is present in a sample it is necessary to concentrate the distillate previously referred to by neutralizing and evaporating on the water bath. Ammonia can be used advantageously, any slight excess of which will have disappeared by the time the solution occupies a small bulk, and to this solution the tests may be applied. The silver nitrate test which is one of the most delicate, has the disadvantage of reacting slightly, particularly upon boiling, with most distillates from foods, due largely to traces of aldehyde. The mercuric chloride test is quite satisfactory where some little formate is present and has the advantage of not being interfered with by aldehydes.

Suggested modification of the ferric chloride test.—The ferric chloride test is very sharp, its great drawback being that acetates produce the same color. In an attempt to differentiate between formic and acetic acids in this test it was found that the formate is insoluble in strong alcohol while the acetate is soluble. In fact many of the metallic formates in addition to those usually mentioned, *i. e.* lead, zinc and magnesium, are practically insoluble in alcohol, this being especially true of the mercury, silver, copper, arsenic, tin, barium, and calcium salts.

The following is the procedure used by the author in the ferric test, making use of this difference of solubility in alcohol of the ferric compounds. The distillate from 100 grams of the sample having been neutralized with ammonia, is evaporated to a few cc., say from 3 to 5; this is transferred to a test tube and is treated with from three to six drops of a ten per cent. solution of ferric chloride, when the characteristic red

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color will be developed in the solution if ammonium formate or acetate is present. Now add 5 cc. of 95 per cent. alcohol for each cc. of solution in the test tube and shake. A precipitate indicates formic acid. If formic acid alone is present when the precipitate has settled out there will be left a clear supernatant liquid; the precipitate, which can be separated by filtration, or better by means of the centrifuge, may be tested to further demonstrate the presence of formic acid. Should there have been only acetic acid present no precipitate is formed and the red color is not destroyed, though somewhat reduced in intensity because of the dilution.

If benzoic acid is present, a precipitate forms upon the addition of the ferric chloride, but this is dissolved when the alcohol is added. In the presence of sulphites the manipulation must be slightly altered as the bisulphite precipitates with ferric chloride and both the neutral salt and the bisulphite are insoluble in alcohol. By making use of this insolubility, that is, by adding absolute alcohol, boiling and filtering, the separation may be effected and the ferric chloride may then be added to the filtrate.

Under ordinary conditions 1/20 of a gram of formic acid gives a very good test, but the presence of an excess of acetate such as would be formed in a neutralized distillate from a food containing vinegar, seriously impairs its delicacy, if it does not altogether prevent the precipitate from forming. If the acetate is present in equal quantities with the formate, the test is not appreciably interfered with and a heavy precipitate forms immediately or in a minute or two, particularly upon shaking.

When twice as much acetate as formate is present there is no precipitation until after a few minutes, and three times as much acetate as formate prevents the precipitate forming for an hour or more. If the acetate is present in much greater excess, no precipitate is formed even upon standing several hours.

To remove an excess of acetate in order that the test may be applied to foods containing acetic acid is a somewhat difficult matter, but the following adaptation of the partial neutralization and distillation method[1], it is believed, will give satisfactory results. This process depends upon the fact that if a partially neutralized mixture of fatty acids is subjected to distillation, the more chemically active acids, or the lower of the series, tend to remain behind as fixed salts. The separation is quite sharp and the ferric chloride test can be applied to the residue of such a distillation with positive results when 0.2 of a gram of formic acid is present. It is therefore suggested that when acetic acid is present in a food to be tested for formic acid the following method be employed.

[1] Wechsler, Monatsh, Chem. 1893, 14, 462. Allen; Commercial Organic Analysis, Vol. 1, 3rd. Ed., Page 487.

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To the distillate obtained by distillation with a current of steam from 100 grams of the sample add from 3 to 8 cc. of normal sodium hydroxide, or such an amount as will probably neutralize the formic acid present, which if added for purposes of preservation will doubtless not be less than 0.20 per cent. The distillate is then subjected to evaporation over a flame, which is continued until the volume has been reduced to about 15 cc.: finish the evaporation on the steam bath, continuing to dryness. Take up with 3 cc. of water and transfer to a test tube: if warm, cool, and then add from 3 to 6 drops of the 10 per cent. solution of ferric chloride followed by 12 to 15 cc. of 95 per cent. alcohol. Sodium formate gives a precipitate but if present in very small quantity or if the amount of added alkali retained a considerable quantity of acetic acid the precipitate will be slow in coming down and it is well for this reason to let the tube stand an hour before discarding as a negative test. Ammonium hydroxide cannot be used in this test, and as sodium acetate is much more insoluble in alcoholic solutions than the ammonium salt it is well to avoid an excess of ferric chloride or an increased alcoholic strength, and better results are obtained when freshly prepared ferric chloride is used.

For the quantitative estimation of formic acid in foods the permanganate or potassium bichromate oxidation methods are not applicable because of the traces of organic matter in the distillate. The method outlined by F. Sparr[1]—originally by Portes and Ruyssen[2]—gives good results, and by it small quantities can be satisfactorily determined. Sulphurous acid however, interferes to some extent when present in appreciable amounts, but when present it may be removed with but a very slight loss of the formic acid by neutralizing the distillate with sodium hydroxide, adding a cc. of concentrated acetic acid, and boiling, when the sulphurous acid will be displaced by the acetic: continue the evaporation until the free acetic acid is removed. The method follows:–

To 25 cc. of the solution to be tested, which should not be more than 1 per cent. in strength, add 5 grams of sodium actate and 200 cc. of a 4.5 per cent. solution of mercuric chloride. Heat from one to one and one-half hours on the bath and make up to 500 cc. The number of cubic centimeters of the filtered solution required to give the red color with one gram of potassium iodide is then determined and from this is calculated the content of formic acid.

Credit is due Mr. S. H. Ayers of the laboratory of A. D. Little, Boston, Mass., for a large part of the work reported concerning the efficiency of formic acid as a preservative.

[1] Z. anal. Chem. 1900, 39, 105.

[2] Compt. rend. 82, 1504.

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NOTES.

Errors Arising from the Use of Cork Stoppers in Quantitative Extractions with Acetone.—The use of cork stoppers for quantitative extractions is generally considered to be unobjectionable, but that such is not the case was recently called to my attention during a series of rubber analyses. The ordinary method of determining the acetone extract with the use of a Soxhlet extractor and cork stoppers was being used, but it was found almost impossible to remove all the soluble extract although the extraction was continued for 90 hours. An examination of the cork stoppers furnished a ready explanation. A white resinous matter had separated out in the cracks of the cork, and a ring of the same material had formed on the stopper and also on the glass where the two came in contact. It was evident that soluble matter was being extracted.

The amount of this soluble matter was determined by cutting up a cork weighing 4.18 grams, placing it in an extraction thimble and extracting with acetone for five hours. 0.2080 grams of a white resinous material was obtained. It is not considered that the extraction was complete but it had proceeded far enough for the purpose of the experiment.

The importance of this matter, especially in rubber analyses where the total weight of extract (in Para rubber) seldom exceeds 0.0600 grams can readily be seen. It is true that cutting the cork into small pieces as in the above experiment made the conditions for the extraction of soluble matter more favorable than in an analysis, but the porosity of the cork is so great that even under actual conditions a very considerable amount would be dissolved. Furthermore an extraction usually continues for a longer time than above and extraction proceeds from two stoppers instead of one.

Disregard of this matter is probably one of the factors which are responsible for the great discrepancies noted between the results of different chemists in the analysis of rubber. The remedy obviously lies in the use of ground glass connections between flask and extractor and extractor and condenser.

EDW. A. BARRIER.

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Otto Dimroth's Paper: "Behavior of Diazonium Compounds Towards Ketonic and Enolic Desmotrophy".—In a recent paper,[1] bearing the above title, Prof. Otto Dimroth describes the behavior of a number of ketonic and enolic compounds towards *p*-nitrobenzenediazonium hydroxide. The enolic compounds yield azo derivatives $HO\overset{|}{C}:\overset{|}{C}N:NR$, whereas the ketonic compounds fail to react. Dimroth discusses the various possible methods of formulating the reaction as follows: (1) $OCCHR' + HON:$

[1] Ber. 40, 2404.

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$NR \rightarrow COCR'N_2R$; (2) $HOC:CH + HON_2R \rightarrow HOC:CN_2R$; (3) $HOC:CH + HON_2R \rightarrow HC:CON_2R \rightarrow HOC:CN_2R$; (4) $HOC:CH + HON_2R \rightarrow (HO)_2CCHN_2R \rightarrow HOC:CN_2R$. This last expression is given incorrectly in Dimroth's paper. The first equation is rejected because of the failure of the ketonic compounds to react. The enolic forms of acetyldibenzoylmethane and of ethyl diacetylsuccinate react readily with the diazonium compound, consequently it cannot be the methane hydrogen which is replaced, and therefore the second of the above equations does not apply. Of the remaining two he favors the latter, but states that it is impossible to decide between them until intermediate compounds, additive or otherwise, have been prepared and investigated.

The object of this note is to call attention to the fact that the present writer alone, and also in conjunction with Alfred Tingle, W. E. Hoffman, Jr., and C. J. Robinson, has prepared a number of such *addition compounds* and has fully discussed their bearing on the problem considered by Dimroth. Most of the results have been published during the past ten years, in a series of papers in the AMERICAN CHEMICAL JOURNAL. The latest paper, in which the question of addition was dealt with at length, was by Bishop Tingle and Robinson.[1] Two other papers bearing on the same subject are now waiting publication and the work will be continued. It may be mentioned that the most interesting additive compounds prepared by Bishop Tingle and his colleagues are those of camphoroxalic acid with hydroxylamine and *p*-bromphenylhydrazine, respectively, and also a a number of derivatives which the acid forms with various secondary aliphatic bases. It follows, therefore, that if Dimroth's reasoning is correct, the problem under consideration may be regarded as having been solved a number of years ago by Bishop Tingle and his co-workers, in favor of the fourth equation given above.

J. BISHOP TINGLE.
McMASTER UNIVERSITY, Toronto, Canada.
July 15, 1907.

NEW BOOKS.

MODERN CHEMISTRY, THEORETICAL AND SYSTEMATIC. By SIR WILLIAM RAMSEY. pp. 127+203. 16-mo. NEW YORK. The Macmillan Company. 1907. Price 70 Cents.

Only a wizard could have packed so much and packed it so comfortably into a little vest-pocket volume of 330 pages. The theoretical part treats of such subjects as, quantitative laws, the properties of gases and of solutions, allotropy, isomerism, stereochemistry, tautomerism, and energetics. In all cases the subjects are handled concisely, yet with perfect clearness. Modern views are emphasized, yet historical perspective is not forgotten. Space is found for opposite illustrations and the whole is

[1] Am. Ch. J. 36, 223 (1906).

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woven together so as to present a miniature picture of chemical theory as it is. One feels on first noting the small size of the volume and the extent of the ground it attempts to cover, that the treatment will of necessity be hackneyed, congested, and charmlessly bare. One is therefor all the more delighted to find that on the contrary, such is the art with which the matter is put together, the mode of handling is fresh, lucid, and attractive, and that the book is, in fact, genuinely readable.

In the systematic part of the volume the limits of space have been met by ingenious classification of the subject. Instead of treating one element at a time in the stereotyped way, the subdivisions are more general. Thus all the methods of isolating elements are discussed together, and a summary of the properties of all the elements follows. Then the common classes of compounds, such as hydrides, halides, oxides, and so forth, are taken up in succession and the various modes of forming the members of each class are described and illustrated. Indicators, the solubility product, alloys, and even the salts of complex inorganic amines receive attention. As in the theoretical portion, the author has managed to include the interesting as well as the fundamental things.

The specialist in other sciences will find in the volume a vivid picture of the outlines of modern chemistry, and the chemist will not fail to derive equal refreshment and profit from its perusal.

ALEXANDER SMITH.

PHYSIKALISCH-CHEMISCHE ÜBUNGEN. DR. W. A. ROTH. a. o. Prof. in Greifswald. Leopold Voss, Hamburg and Leipzig 1907. XII+174 pp. Cloth, price 5 Marks.

This book, as its title indicates, and the author is careful to further emphasize in his preface, makes no claim to compete as a reference book with the larger manuals on the subject such as the Ostwald-Luther "Hand-und Hilfsbuch," but endeavors to present in concise and easily intelligible form, fairly specific directions for a set of laboratory exercises together with such discussion of the general principles involved as to bring out the full pedagogic value of the practical work itself. In pursuance of this idea the author has omitted practically all references to the original literature and has compiled the accompanying tables to meet simply the immediate needs of the text. The book we are told represents, essentially the work of the elementary course ("Kleinen Praktikums") in physical chemistry conducted by Prof. Nernst in Göttingen and later in Berlin.

The chief headings in their order are: Introduction, the fundamentals of physical measurements and calculations, 12 pages. Determination of density of gases, liquids and solids, 23 pages. Molecular weight of dissolved substances, 15 pages. Thermochemistry, 18 pages. Determination of optical constants, 13 pages. Chemical statics and kinetics, 9 pages. The remaining third of the book is devoted to Electrochemistry,

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subdivided as follows: Fundamental principles, 18 pages. Conductivity, 13 pages. Faraday's law and migration numbers, 9 pages. Electromotive force, 15 pages. Electro-static measurements, including radio-activity, 9 pages. Tables, 3 pages.

The selection and proportioning throughout is good and the book contains much in its choice of experiments and mode of carrying them out that should prove helpful to those in charge of such courses.

Anyone who has attempted to break away from the meager assortment of stock experiments used as illustrations over and over again by the different authors of physico-chemical text books knows the difficulty of finding suitable substitutes which can really be used effectively under the limitations of time and equipment which usually obtain in an elementary laboratory course. It is perhaps in this matter that the present book will be of most service to teachers in this country.

On the whole the book presents an admirable treatment of the subject for the purpose the author had before him. F. G. COTTRELL.

THEORIES OF CHEMISTRY, BEING LECTURES DELIVERED AT THE UNIVERSITY OF CALIFORNIA, IN BERKELEY. BY SVANTE ARRHENIUS. Edited by T. Slater Price. Price, $1.75. Longmans, Green & Co., 1907.

The appearance of these lectures by Arrhenius, and the previous appearance of a similar set by Ostwald, has made the past year one singularly rich in the historical and philosophical treatment of general and physical chemistry. Coming as they do from such master hands, treating similar problems, and each full to overflowing with the genius of their authors, they can not fail to supplement one another, and to exert enormous influence for good.

The lectures of Arrhenius are not only more special than those of Ostwald in the material treated, but also differ in the general point of view. The two sets, in fact, represent ideals of opposite extremes in methods of thought and treatment. Ostwald with his love of historical research, seeking out the originator of each fruitful thought, and placing each concept on a hypothesis-free foundation; Arrhenius developing and basing his ideas upon the conventional hypotheses which are, and have been, in common use. Both will be read widely because of the authority and pre-eminent station of their authors, but probably at the present day the method of Arrhenius will be the more popular, because more conservative and less startling. It is not likely to be so in the future, however; then, and in the opinion of the reviewer this day cannot be far distant, the method used by Ostwald will be accepted as the simpler and clearer.

In few words, Ostwald shows how the things which have been developed *could* be developed without the aid of hypotheses; Arrhenius, on the other hand, shows how these things *have been* developed, and how

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logical has been the growth of our modern theories from the older ones.

This book cannot be too highly recommended to those interested in physical chemistry. The sane view of each question considered, the excellent exposition of each theory, and the clear, close reasoning with which the fallacy of often misunderstood points is exposed, together with the excellent English, make the book one that it is a pleasure to read. The chapter headings are as follows: Introduction—The use of theories; Old hypotheses in chemistry; Existence of hydrates in solution; Discussion of the validity of Dalton's law; Electrical force between the atoms; The law of Faraday; Chemical valency and affinity; The development of the doctrine of valency; Composition of the atoms.—Electrons; Theory of gases; Chemical kinetics and statics; The influence of temperature and pressure—Dissociation; Osmotic pressure—General laws for dissolved substances; Electrolytic dissociation; Problems to be solved—Objections.

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L. H. BAEKELAND.

HYDROMETALLURGY OF SILVER—WITH SPECIAL REFERENCE TO CHLORODIZING, ROASTING AND THE EXTRACTION OF SILVER BY HYPOSULPHITE AND CYANIDE SOLUTIONS. BY OTTOKAR HOFMANN. pp. V+345. 83 illustrations. Hill Publishing Co., New York, London: 1907. Cloth, $4.00.

The author of this book introduced the Patera Process of leaching silver ores with hyposulphite solutions in 1868 in Mexico. Since that time he has been prominent in this branch of metallurgy and has won for himself the enviable position of an acknowledged authority.

The book under consideration is on the whole a record of personal experience based upon established principles. There is presented not a general treatise like that of H. F. Collins,[1] in which all that leading workers have accomplished is brought together in a most satisfactory manner, but a book resembling more the well known volume of the late C. A. Stetefeldt.[2] While Hofmann aims to bring out mainly the full details of practice and is antagonistic to the Russell modification of the Patera process, Stetefeldt lays more stress upon chemical conceptions and is the acknowledged defender of the late E. H. Russell. The three publications supplement one another and about cover the field.

In addition to the Patera process which, with chlorodizing roasting, takes up 255 of the 328 pages of text, the Augustin and Ziervogel pro-

[1] "Silver," Griffin & Co., London, 1900.

[2] The Lixiviation of Silver Ores with Hyposulphite Solutions, author, New York, 1895.

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cesses receive each a passing notice of one page as is the case with the Freiberg method of leaching roasted silver-bearing copper matte, while the author's interesting modification of the last process is treated with considerable detail in 19 pages. Cyanidation, covering 41 pages, is represented mainly by a full abstract of the excellent paper of T. H. Oxnam [1] on the treatment of auriferous silver ores at Palmarejo, Mexico. Electrodeposition of precious metal from cyanide solutions, especially important in silver-metallurgy, is not touched upon.

To take up a few special features. The first 152 pages deal with chlorodizing roasting. After a brief general statement of principles and of behavior of the leading minerals, there is given an important chapter on the fine crushing of ore and how it has to be governed by the character of the component minerals with regard to subsequent chloridation and success in leaching. The discussion of the amount of salt required and the time of addition brings out many points as to chloridation and volatilization which are not generally known, in fact, will be new to most readers.

In the chapter on furnaces, the leading ones that have been proposed and used are assigned their proper places; the mode of operating is treated in its different aspects with the results to be expected and the results that have been obtained. The author's designs for dust-chambers with a special discussion of the correct manner of handling argentiferous zinc-lead ores and calcareous ores closes this chapter which stands forth preeminently as the most important one of the book. Tank-lixiviation with precipitation and working up of precipitate is taken up with working drawings of apparatus which give a clear conception of modern practice.

In studying the chapter on trough-lixiviation, the reader obtains the impression that this method, invented by the author, is an accepted improvement on tank-lixiviation, which it is not. The description ought to be read in connection with Stetefeldt's review of the method.

The critical remarks upon the Russell and Kiss processes, while brief, are a relief in view of the many laudatory papers that have been written about them.

While the Patera process has seen its best days on account of the encroachment of smelting upon leaching and of the growing importance of cyanidation, it will retain some of its former importance for a considerable time. The metallurgical profession is therefore under much obligation to the author for having brought together in book form some of the leading features of his wide experience. H. O. HOFMAN.

BOTANY AND PHARMACOGNOSY. By HENRY KRAEMER, Ph. B., Ph. D. Second revised and enlarged edition. J. B. Lippincott Company, Philadelphia.

The new edition is twice the size of the old one, the number of illus-

[1] Tran. Am. Inst. of Min. Eng., 1906, 36, 234-87.

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trations has been more than doubled, and in many other respects generally improved. This has been done without changing the arrangement of the subject matter. The work is divided into three parts. The first treats of botany, the second of pharmacognosy and the third of reagents and microscopic technique. Under botany the first 90 pages are devoted to the structure and general characteristics of the different groups of plants, beginning with the lower forms of plant life, the algae, and ascending to the higher forms, the spermophites, or seed plants. The next 65 pages treat of the "Outer Morphology of Angiosperms" in the order of root, stem, leaf, flower, fruit and seed. The following 67 pages treat of the "Inner Morphology of the Higher Plants," taking up the plant cell, its contents and forms; then follows the structure of different parts of plants. The next 180 pages are devoted to the "Classification of Angiosperms Yielding Vegetable Drugs." The habitat with a short description of each plant is given, and also the active constituents. The last 14 pages of part one are given to the "Cultivation of Medicinal Plants."

The part devoted to Pharmacognosy is divided into two chapters. The first 278 pages are given to the study of "Crude Drugs," giving source, description and constituents. The following 94 are given to a systematic, microscopical study of "Powdered Drugs and Foods."

Only the last eight pages are devoted to "Reagents and Microscopical Technique."

The entire work is beautifully illustrated with 321 plates and about 1500 figures. These are distributed throughout the text, which is a decided improvement over the former edition, where the illustrations were given in a separate part of the work. The present arrangement permits of the ready comparison of the illustrations with the subject matter. Most of the illustrations are from fine pen drawings, while others are half-tone reproductions, some of which are very good, while others are inferior, lacking in detail, due doubtless to improper exposure.

In general the technique of the work is fine, and the author and publishers are to be congratulated upon the results of their efforts. The book is one that should be in the hands of every one interested in the study of botany and pharmacognosy. A. B. STEVENS.

A HANDY BOOK FOR BREWERS. By HERBERT EDWARDS WRIGHT. Third edition, 562 pages, New York: D. Van Nostrand Company.

The principal aim of the author has been to give the conclusions of modern research in so far as they bear upon the practice of brewing, in such a form that a novice of fair intelligence may understand them. The trained chemist or physiologist however, will also be benefited by the study of this book. In fact between these branches of pure science and the brewing industry a very fertile reciprocal action has always been

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going on. It is well known how much the chemistry of carbohydrates and the physiology of plants are indebted to English brewing chemists. In dealing especially with the methods of brewing used on the British Isles the author quite naturally gives a full account of the work carried on by his compatriots, but he reports with equal conscientiousness the researches made abroad, and evinces great impartiality in judging also such theories as do not agree with the views generally held by English brewing scientists at the present moment. In one instance, speaking of scientific work done in America, the author says: "we cannot conceal from ourselves that with the lighter gravities of beers now in vogue the Trade must aim at utilizing every method for securing not only the best but the most profitable results.....May they not in some modified form be utilized here?" Great care has been taken to bring the work up to date, even the latest researches of the French scientists on saccharification of starch being mentioned. The author does not live to see this last edition of his work printed. He died within a few hours after dictating the preface; but he has raised for himself a lasting monument in his excellent book. ROBERT WAHL.

JAHRBUCH DES VEREINS DER SPIRITUS-FABRIKANTEN IN DEUTSCHLAND, DES VEREINS DES STÄRKE INTERESSENTEN IN DEUTSCHLAND UND DES VEREINS DUTSCHER KARTOFFELTROCKNER. SIEBENTER JAHRGANG, 1907. Berlin. PAUL PAREY, 1907.

This annual published in the interests of the societies named is really a report of the work done under the direction of the Institute für Gährungs gewerbe in Berlin, the work of the several societies and the matter published in the Zeitschrift fur Spiritusindustrie. This year a third society has been included in the combination the work of which is reported, and so covers in every way the utilization of the potato crop in Germany. The new connection is intended to cover the preservation of the crop for continuous use in the manufacture of the several ultimate products of the industries, starch, glucose and alcohol.

The Jahrbuch is authoritative in the highest degree and is intensely devoted to the industries represented. It reports faithfully all the advances made in the study and investigation of potato culture, starch making, the production of yeast and its biology, reviewing all the advances of any importance made in a scientific or technical way in the promotion of the industries. It seems rather remarkable however that no mention is made of the rather startling discovery of Ehrlich of the transformation of the amino-acids to amyl alcohol through the influence of the saccharomyces in fermenting liquids and media. However, the book contains so much of value to those interest-

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ed in the utilization of starch producing materials, that it should find place in the library of every technologist and chemist devoted to any of the industries dependent upon these materials as sources of supply.

WM. MCMURTRIE.

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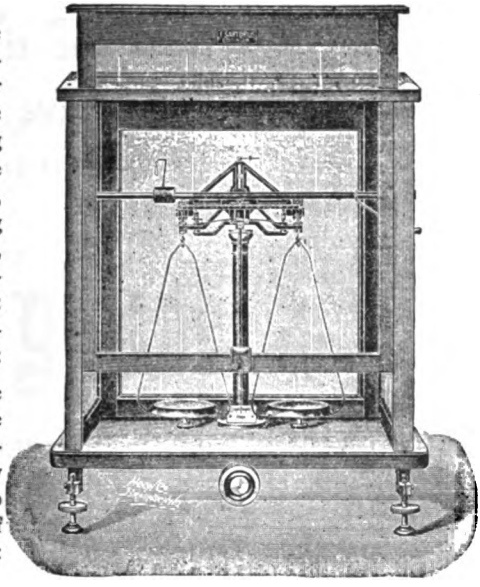
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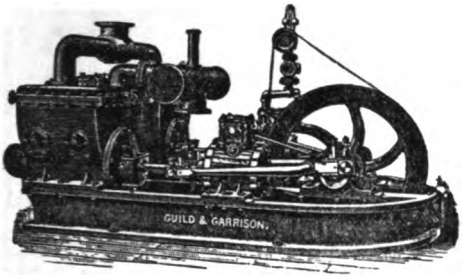
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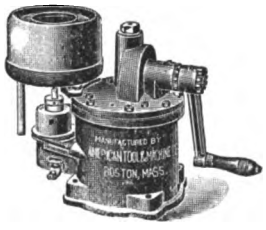
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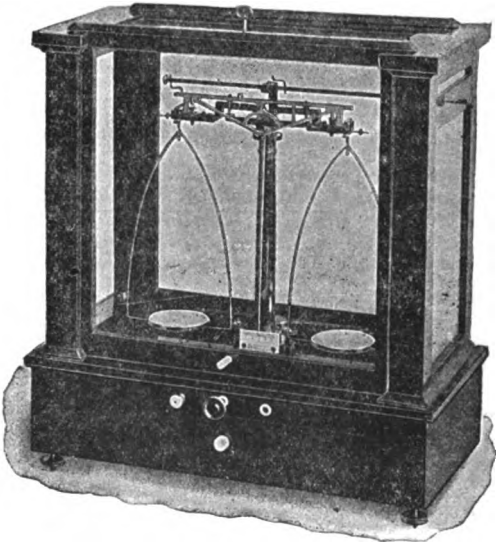
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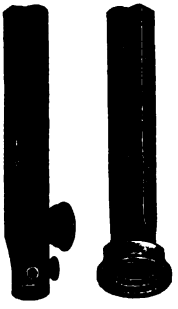
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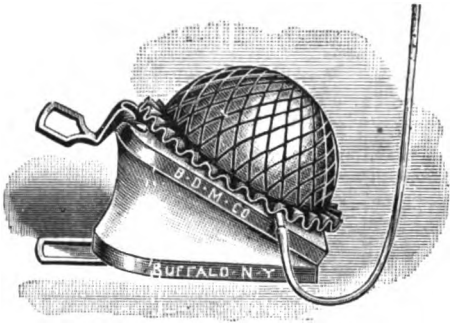
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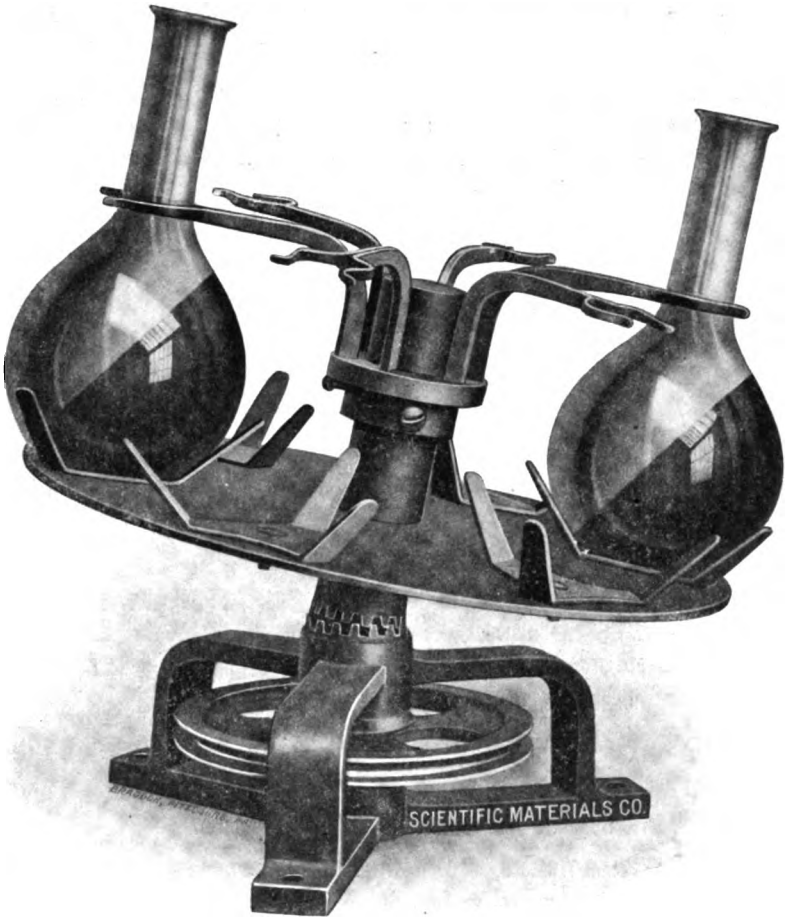
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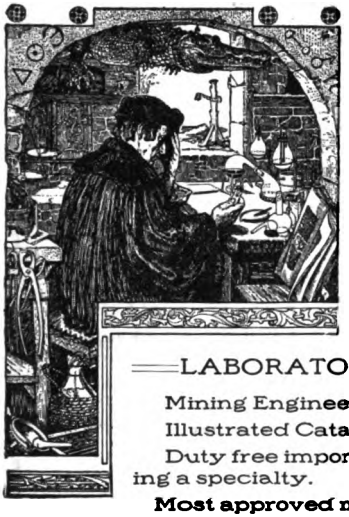
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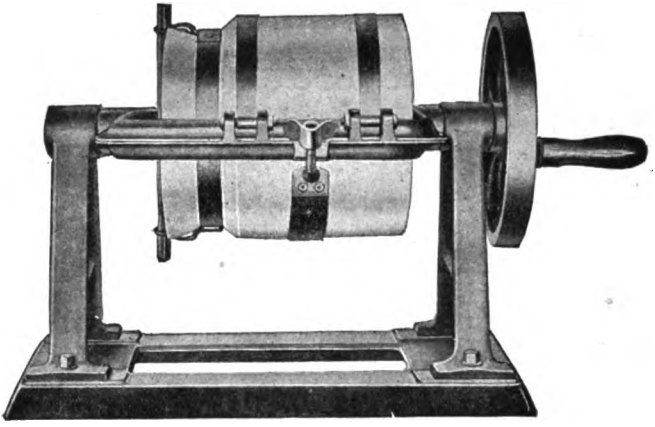
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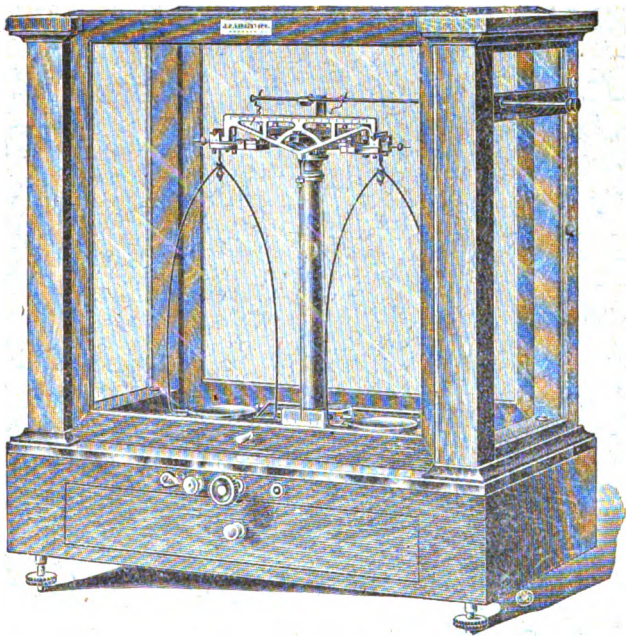
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THE CORROSION OF IRON AND STEEL.[1]

BY WILLIAM H. WALKER, ANNA M. CEDERHOLM AND LEAVITT N. BENT.

Received June 14, 1907.

Some time ago an investigation was undertaken in this laboratory with a view to throwing some light upon the much discussed question as to whether wrought iron is more resistant to corrosion than is steel. To this end a relatively large quantity of pure iron was prepared, and with this as a basis, alloys of iron and varying amounts of the different elements occurring in commercial iron and steel were made by melting the constituents in alumina crucibles heated by an electric furnace operating under a high vacuum. In studying the specimens so produced, it early became apparent that a more complete understanding of the factors which occasion corrosion and the conditions under which corrosion proceeds was necessary in order that our results could be intelligently interpreted. A study of the literature on the subject showed it to be so voluminous and so altogether contradictory, that as a first step in our investigation of the general subject of the influence of the constituents of iron or steel upon its corrosion, we decided to determine, if possible, the mechanism of the reactions by reason of which corrosion takes place.[2]

Theories of Corrosion.

The more important theories of the corrosion of iron and steel which seem to be worthy of discussion may be considered under three heads, the first, when taken up chronologically, being the *carbon dioxide theory*. Although the subject of corrosion had been investigated by a number of

[1] Read before the New York Section, May 1907.

[2] Since this part of the work was undertaken we have learned that Dr. Allerton S. Cushman, Assistant Director, Office of Public Roads, Washington, has also been investigating this subject. Although contemporaneous, the investigations have been carried on entirely independently, except in regard to the ferroxyl indicator, and it is believed that Dr. Cushman's work will be found to confirm in many respects the results herein recorded.

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workers, Dr. Grace Calvert in 1871 seems to have been the first to have carried on a systematic study of the factors entering into the reaction, and concludes that at least three reagents are essential, viz. water, oxygen and carbon dioxide. This work received a complete endorsement at the hands of Crum Brown in 1888, who summarized the successive changes in the process of corrosion in the following equations:

$$4(Fe + H_2O + CO_2) = 4FeCO_3 + 4H_2$$
$$4FeCO_3 + 6\,H_2O + O_2 = 2Fe_2(OH)_6 + 4CO_2$$

Two important facts regarding corrosion may be so easily explained by this theory that it has been very generally accepted by textbook writers and thus gained credence. These facts are, first, that the presence of carbon dioxide accelerates corrosion, and, second, that alkalies such as calcium hydroxide entirely prevent corrosion.

The latest and possibly most convincing work to be done on this subject is that of Gerald T. Moody[1], which apparently proves that no corrosion of iron will take place without carbon dioxide.

Moody's principal experiment consisted in exposing a bright piece of pure iron immersed in water to a stream of oxygen, the utmost precautions having been taken to exclude the presence of carbon dioxide. The different parts of the apparatus were connected by glass seals and in order to free them from carbon dioxide, air, after passing through a most elaborate washing and purifying system, was drawn for three weeks through the apparatus. Notwithstanding these precautions, rust in small amounts was found to develop on the specimens after a few days. When, however, air from which the carbon dioxide had not been absorbed was drawn through the water in which the iron was immersed, corrosion rapidly increased.

Moody concluded that the very small amount of rust which he had observed before the unwashed air was led in, was due to a trace of carbon dioxide which had been introduced with the piece of iron. He therefore immersed his specimens in a one per cent. solution of chromic acid in order that they might be protected from the carbon dioxide until the apparatus had been swept entirely free from this gas. After again drawing carbon dioxide-free air through the system for three weeks, the chromic acid was displaced by passing through the tube containing the iron a large quantity of pure water, introduced in such a manner as to insure no contamination with carbon dioxide. This water entirely removed all traces of this protective chromic acid solution. Carbon dioxide-free air was then drawn through the water and over the iron for five weeks and at the end of that period no rust could be observed. The connection between the washing system and the specimen was then

[1] J. Chem. Soc., (London) 89, 720.

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broken and unwashed air drawn through the water. Very considerable corrosion was observed after three days.

Electrolytic Theory.—In 1903, W. R. Whitney[1] published the results of an investigation, which furnished data on which he based a theory of corrosion in accordance with the conceptions of Nernst and the modern theory of solutions. In accordance with this theory metals can dissolve only by entering the solution as electrically charged ions. This escaping tendency of a metal is measured by a force known as the electrolytic solution pressure, which will operate in any solution until counterbalanced by the osmotic pressure of the metal already in solution. In passing into the ionized state, the ions assume their positive charges while the residual negative charges remain upon the metal. Action is therefore immediately arrested on account of the difference of potential which would exist between the positively charged ions and negatively charged metal. In the case when iron is immersed in a solution of copper sulphate, there are present the positively charged copper ions which have a smaller solution pressure than the positively charged iron ions, and hence when the former are attracted to the negatively charged metallic iron their charges are neutralized and metallic copper is precipitated. Since its solution pressure is less than that of the iron, there is little tendency for the copper ions to again dissolve in the presence of iron, and the action continues.

Hydrogen acts as a metal and has an electrolytic solution pressure which places it between iron and copper in the series of metals. Iron placed in a solution containing hydrogen ions will therefore dissolve at a velocity dependent in general upon the concentration of the hydrogen ions and the ease with which the gas can be liberated upon the iron surface. Water is dissociated to a small extent into hydrogen and hydroxyl ions and hence, if this theory holds, iron should pass into solution to a slight extent, with the liberation of an equivalent amount of hydrogen. Any reagent which increases the concentration of the hydrogen ions, such as an acid, will increase the corrosive action, while any agent which will decrease this hydrogen concentration will inhibit corrosion. In this way is explained the protecting effect of the alkalies and of any substance, for example, borax, which by hydrolysis yields hydroxyl ions, inasmuch as the product of the hydrogen and hydroxyl ions must remain a constant. The formation of rust is thus seen to be a secondary action brought about by the oxidation of the already dissolved iron by the action of atmospheric oxygen. The role of carbon dioxide is but that of any acid, increasing by its presence the concentration of the hydrogen ions and to this extent accelerating the action.

[1] This Journal, 25, 394.

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Hydrogen Peroxide Theory.—Dunstan, Jowett and Goulding[1] repeated the work of Whitney and failed to get any evidence that iron dissolved in pure water free from oxygen and carbon dioxide. They therefore considered this theory untenable and advanced a theory based upon the fact that when some metals oxidize in water, hydrogen peroxide is frequently formed. The chemical action taking place when iron corrodes in water with access of oxygen is represented by these authors as follows:

$$\begin{aligned} Fe + H_2O &= FeO + H_2 \\ H_2 + O_2 &= H_2O_2 \\ 2FeO + H_2O_2 &= Fe_2O_2(OH)_2 \text{ (rust)} \end{aligned}$$

Although a great deal of experimental work was done, these investigators failed in every instance to get evidence of the presence of hydrogen peroxide in the oxidation of iron. This theory explains the fact that when zinc corrodes in water hydrogen peroxide may be detected, by the supposition that hydrogen peroxide can exist upon the surface of zinc, while when iron corrodes the hydrogen peroxide is incapable of existence on the surface of the iron long enough to make detection possible. Support for this idea is found in the fact that in every case, those reagents which inhibit rusting, are also substances which decompose hydrogen peroxide.

Experimental.

Evidently the first question to be settled is—Is carbon dioxide essential to corrosion? To this end we repeated the experiments of Moody, duplicating his apparatus and method in every possible particular. In general, our observations coincide with his. Our explanation of the phenomena observed, however, differs radically from his. It is well known that pure water attacks with considerable ease all glass except that which has been most carefully prepared, producing an alkaline solution. It is also well established that in pure water a relatively small amount of free alkali will inhibit rusting. We therefore again repeated Moody's experiment, but constructed the apparatus so that a little phenol-phthalein could be introduced after the water had been passed through the tube containing the iron. Both the water which was on the iron and also that which had passed over the iron into a flask beyond showed a distinct bright red when the indicator was added. When air containing carbon dioxide was passed through the solution this alkali was converted into the acid carbonate and the corrosion accelerated. When Jena glass which had been steamed for two days was employed, the iron corroded almost as readily as when left in the open air. We feel satisfied that in our experiments (and we believe the same to be true of Moody's) the tardy corrosion of the iron was due to the inhibiting effect of the free

[1] Chem. Soc. (London) 84, 1584. (1905.)

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alkali present, and that iron does rust in the presence of air containing no carbon dioxide.

All those experiments of Moody in which chromic acid was used are rendered worthless, so far as showing the preservation of iron in the absence of carbon dioxide is concerned, by the fact, apparently overlooked by Moody, that immersing iron in chromic acid or potassium dichromate will render it relatively passive. We have repeated these experiments a number of times, carrying on simultaneously a check experiment in which we treated a specimen of the same iron with a portion of the same chromic acid solution, but drew ordinary unwashed air through the apparatus. No difference could be observed in the latter case. The fact that iron is preserved by solutions of the chromates was mentioned by Wood[1] in 1894, and later by a number of writers including Moody himself. No one seems to have noticed, however, that the passivity imparted to iron by such a solution is retained by the specimen after it is washed with pure water and dried. Without going further into this phenomenon we can but give it as our opinion that the apparent noncorrosion of iron in the absence of carbon dioxide, is due, not to the fact that no carbon dioxide is present, but to the fact that the iron is protected by the as yet not clearly understood condition of passivity, brought about by its immersion in a chromic acid solution.[2] A further proof that carbon dioxide is not essential to corrosion will be given later under the consideration of the influence of oxygen on corrosion.

The failure of the writers already noted to duplicate the results of Whitney, probably accounts for the fact that the electrolytic theory has not been more generally accepted. Even so valuable a textbook as "General Inorganic Chemistry" by Alexander Smith, does not mention the possibility of this explanation, although it makes very general use of the newer theories of chemistry involved in Whitney's work. The carbon dioxide theory and the peroxide theory of Dunstan are given sufficient space, while the electrolytic theory is ignored.

Evidently the theory of Whitney must stand or fall with the truthfulness of his statement that iron dissolves in pure water entirely free from oxygen and carbon dioxide. Although we employed a number of types of apparatus in studying this question, the following is both very simple and satisfactory. A round bottom Jena flask of about one liter capacity is inverted on a nozzle supplying live steam, for at least twenty-four hours. This insures the removal of any easily soluble alkalies, which

[1] Trans. Am. Soc. Mech. Eng. 16, 384.

[2] Since the above was written, a short notice of an article by Wyndham R. Dunstan appeared in Chem. Soc. 22, 63, in which the experiments of Moody without chromic acid have been repeated. Dunstan confirms his previous results and those stated above, in that iron rusts freely in the presence of oxygen and water containing no carbon dioxide.

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would otherwise destroy the neutrality of the liquid. The flask is fitted with a carefully cleaned rubber stopper through which extends a glass tube drawn down to a moderate-sized capillary at its upper end. The flask is three-fourths filled with ordinary distilled water (not conductivity water) which has previously been boiled for several hours in a block-tin heater. The water in the flask is boiled for about ten minutes and while steam is still rapidly passing out of the opening, the stopper is removed and a piece of bright iron introduced. The stopper is again inserted, the boiling continued for another ten minutes and while boiling the capillary is sealed. The flask is allowed to cool after thickly coating the stopper with molten paraffin. If this experiment be carefully performed, no action will be observed, the iron remaining bright and the water clear even after standing several days. When the stopper is removed and the water concentrated in a platinum dish, using every precaution to prevent contamination from dust, a strong test for iron can always be obtained by the addition of a drop of ferrocyanide or sulphocyanate of potassium solution.

Thinking that possibly enough gas had been occluded in the iron to effect the reaction, the above experiment was repeated a number of times under conditions which allowed of introducing pieces of iron which had been heated to low redness and cooled in hydrogen. In every case the presence of iron was easily detected when the content of the flask was evaporated to a few drops.

This experiment was again repeated with the additional precaution of using water which had been allowed to stand for a number of days over a large quantity of spongy metallic iron, the water being introduced into the reaction flask by distilling it from the iron in an atmosphere of hydrogen. Notwithstanding all these precautions, a distinct test for iron was obtained after the water had been concentrated. In all these experiments "blanks" were run which in no case showed that sufficient iron had been dissolved either from the glass or from the platinum to furnish the test which was obtained.

We therefore support Whitney in his statement that iron will dissolve in water which contains not more than a trace of electrolyte, no oxygen, and only that amount of carbon dioxide which is not retained by a strong alkaline hydroxide. In explanation of the failure of the investigators previously cited to detect dissolved iron, we would state that usually it is not possible to obtain an indication of iron with potassium ferricyanide, for example, in the water as it comes from the flask; concentration is generally necessary.

Ferroxyl Indicator.—That the corrosion of iron is an electrolytic phenomenon is shown by a very simple experiment devised by Dr. Allerton S. Cushman and ourselves. A piece of iron is immersed in ordinary

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water to which has been added a little phenolphthalein and a trace of potassium ferricyanide. Within a very few minutes the iron is seen to divide itself into zones or surfaces which exhibit opposite polarity. Those portions where the iron is anodic will become coated with a precipitate of Turnbull's blue, owing to the escape of the iron ions at those points. Those portions on which hydrogen is being liberated, acting as cathodes, will become bright red owing to the formation of hydroxyl ions. This action may be more easily studied if this reagent (for which Dr. Cushman has proposed the name "ferroxyl") be thickened by the addition of neutral gelatin or agar-agar. We will return to this phenomenon later in this paper.

Function of Oxygen.—The rapidity with which iron will pass into solution in water depends not only upon the electrolytic solution pressure of the iron and hydrogen, and the osmotic pressure of the iron ions already in solution, but also upon the "excess voltage" (überspannung) which is required in order that the hydrogen ion which passes from the ionized condition may be set free.[1] In this case there is a counter electromotive force which must be overcome before the hydrogen can be liberated. It is possible, therefore, that the quantity of iron which can dissolve in water is limited to that amount which is equivalent to the hydrogen necessary to polarize that portion of the specimen which acts as the cathode. If this is the case, we should be able to make this solvent action continuous by the addition of any reagent which will depolarize the hydrogen-covered cathode portion. This reaction may be shown by the following very simple apparatus.

Two unglazed porcelain cups are placed concentric with each other and within a small Mason fruit jar, in the zinc top of which is soldered a small piece of copper tubing. The three vessels are filled with hundredth-normal potassium chloride solution free from oxygen and carbon dioxide, and the whole placed upon a hot plate of a temperature to insure continuous boiling. Two pieces of clean, pure iron, joined by an iron wire, are introduced into the central and outside compartment and the whole while still boiling is sealed by screwing on the metallic cap. Hydrogen is allowed to enter the jar as it cools in order to relieve the vacuum and prevent leakage of air. Such a cell may be maintained many hours without dissolving enough iron in either compartment to be detected by potassium ferricyanide in its unconcentrated condition. When reduced to a few drops, however, iron may always be shown to be present. Portions of each iron plate may be assumed to be anodic with iron tending to go into the ionized form, and other portions cathodic, being polarized by a film of hydrogen. If, now, a substance which will dissolve away the hydrogen be added to one compartment, the cathodic portion of the iron

[1] Nernst, Theoretische Chemie, 5th Ed., p. 712.

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contained therein should be depolarized and the action should result in the solution of the anodic portions. Since the two pieces of iron are short-circuited above by a wire and below by the electrolyte, that piece which is continually depolarized would be expected to become the cathode, and the other the anode. Hydroxylamine serves as such a depolarizer and from an apparatus as above described, after standing for forty-five hours at room temperature the following results were obtained:

	Blank	Hydroxylamine
Increase in weight of cathode	0.0005 grs.	0.0380 grs.
Decrease " " anode	0.0002 grs.	0.0393 grs.

When a five per cent. solution of potassium dichromate is used as a depolarizer, and the cell allowed to stand at room temperature for 40 hours the results were:

	Blank	$K_2Cr_2O_7$
Increase in weight of cathode	0.0001	0.0212
Decrease " " " anode	0.0000	0.0217

By passing a stream of hydrogen gas through all three cups iron will not dissolve in six hours sufficiently to give directly the ferricyanide test. If the hydrogen stream in one compartment be replaced by oxygen, iron will immediately begin to dissolve at an appreciable rate in the other compartment, separated though it is by the intermediate compartment through which hydrogen is passing. The dissolved iron in the anode compartment remains in solution as a ferrous salt while the cathode compartment becomes strongly alkaline. If the porous cells be withdrawn, the iron at once oxidizes and is precipitated as brown ferric hydroxide.

Mr. J. A. Collins, in a thesis presented at the Institute in 1898, noted the fact that if a piece of iron and a piece of magnetic oxide be immersed in water and connected through a voltameter, a very appreciable current would flow through the system with the iron as anode. To determine whether oxygen was a factor in this process the following experiment was performed: In a Jena flask containing hundredth-normal potassium chloride were suspended by fine platinum wires a piece of pure iron and a piece of magnetic oxide. These suspending wires were connected through a silver voltameter. By fitting the flask with a stopper containing gas inlet and outlet tubes, the operation could be carried on in either a vacuum, or in any desired atmosphere. When all air and carbon dioxide were expelled by long boiling, and the flask cooled under conditions which preserved the vacuum, no current passed through the voltameter upon closing the switch. When connected through a Lippman electrometer, however, a difference of potential between the two pieces was apparent. The electromotive force of the system is obviously not sufficient to furnish the "excess voltage" necessary to liberate the hydrogen on the magnetic scale, and while there exists this marked difference of potential,

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no appreciable current passes. If the concentration of the hydrogen ions be increased, as can be accomplished by saturating the water with carbon dioxide, the electromotive force is then sufficient to overcome this resistance and a measurable current is obtained, the iron passing into solution. If, on the other hand, air free from carbon dioxide be passed into the flask, the cathodic film is depolarized by the oxygen and the iron dissolves. As a secondary reaction, the oxygen oxidizes, and the hydroxyl set free at the cathode precipitates the dissolved iron with the deposition of rust; this formation of rust is a factor in corrosion, however, only in so far that the concentration of the iron ions is kept very low and hence its osmotic pressure is negligible.

The influence of the depolarizing action of oxygen may be conveniently studied by using the ferroxyl indicator. For example, in a beaker may be placed a porous earthen-ware cell and the whole filled with ordinary water containing phenolphthalein and a very little ferricyanide. If a piece of iron be placed within the cell and connected by means of an iron wire with a piece of platinum in the outside compartment, immediate action takes place, deep red appearing on the platinum and a coating of blue precipitating on the iron. If, however, the platinum be heated in an alkaline pyrogallate solution, washed in boiling distilled water, and while wet used as the cathode in the cell, no action will take place for a number of hours. Only as the platinum takes up oxygen from the atmosphere, does the reaction become apparent.

The influence upon the rate of solution of iron which different metals exercise when connected by a metallic conductor with the iron, is also easily shown by this method. Those metals in the electrochemical series more negative than iron influence the action, not in proportion to their relative position in the series, but rather in proportion to some other property, possibly their ability to occlude or condense oxygen. On the other hand, aluminum is much less active in protecting iron than is zinc although it is more electro positive, while manganese completely reverses the polarity, making the iron the cathode and itself dissolving rapidly with the formation of brown manganese hydroxide.

Another conception of this action which differs only in the point of view from the above, is to consider the metal which acts as a cathode, for example, the platinum, as an oxygen electrode, and that the current flowing through the circuit (on account of which the iron dissolves) is due to the solution of oxygen and the formation of hydroxyl ions charging the solution negatively, and thereby requiring a solution of iron at the other electrode to bring about electrostatic equilibrium. When viewed in either of these two lights, the action should be proportional to the concentration of oxygen in the solution, and hence, according to the laws of Henry and Dalton, to the partial pressure of the oxygen in the

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atmosphere above the solution. An experiment to test this conclusion was performed as follows: A number of Jena flasks were partly filled with boiled water and connected by means of a by-pass to a reservior filled with definite mixtures of oxygen and nitrogen, freed as far as possible from carbon dioxide by being washed through strong potassium hydroxide and stored over barium hydroxide solution. When the water in the flasks was boiling violently, equal weights of pure iron were introduced and after ten minutes furthur boiling, the exit tubes were sealed, and by means of the by-passes, each flask as it cooled drew from the reservoir with which it was connected an atmosphere of known composition. Two or three times each day the gas over the solution was changed by passing through the flask a quantity of gas from the reservoir. At the end of a few hours the difference in the rapidity with which the iron was attacked was easily apparent, and after standing for four or five days the wire in each flask was cleaned and weighed. Any oxide which adhered to the wire was reduced in hydrogen and the wire again weighed. The loss of iron was in this way calculated and the results shown in the plot. The rate of the reaction is thus seen to be a direct function of the oxygen pressure and it is to be noted that the curve passes through the zero point. Only that amount of carbon dioxide which will not be absorbed by strong caustic alkalies could have been present, and this amount must have been constant in each flask. If the presence of carbon dioxide is an important factor in corrosion, it is difficult to understand why the solvent action should be so independent of the amount of carbon dioxide present. Although the same weight of iron was added to each flask there was not the same area undergoing active corrosion in each case. There were always clearly defined cathodic portions on each wire, which remained perfectly bright and on which the hydrogen was being deposited and the oxygen absorbed. These differed markedly in the different specimens but did not seem to bear a definite relation to the pressure of oxygen. When phenolphthalein was present, the bright spots were seen to continue to maintain a red zone in the solution around them. This irregularity in the area of iron actually attacked, accounts in some measure for the irregularities in the position of points not falling on the straight line in the plot.

The fact that the accelerating action of increased pressure of oxygen may be looked upon as due to an oxygen electrode, has an interesting bearing upon Dunstan's theory of the intermediate formation of hydrogen peroxide. Richarz and Lonnes[1] decomposed water saturated with air by passing through it, between platinum electrodes, a current of low electrode density. They found that at the cathode the hydrogen was to a large extent not liberated as such but that it combined with the dis-

[1] Z. physik. Chem. 20, 145.

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solved oxygen to form hydrogen peroxide. These are exactly the conditions which obtain upon the cathodic portions of iron undergoing corrosion, except that here we have iron instead of platinum. The appearance of hydrogen peroxide is therefore to be expected, provided it can exist on an iron surface. Dunstan could detect it when zinc corroded but failed to get a positive reaction in the case of iron. Dunstan explains the generally recognized inhibiting effect of the alkalies, potassium dichromate, etc., by the fact that they all instantly decompose hydrogen peroxide. If some condition already exists upon the surface of the iron such that hydrogen peroxide cannot exist, and if hydrogen peroxide is a step in the formation of rust, it is difficult to see what influence either for or against corrosion substances can have which also destroy hydrogen peroxide. The peroxide if formed at all, can be formed only when hydrogen is being oxidized by the dissolved oxygen, and the latter reaction takes place, as we have shown, on points separated from the points at which iron is passing into solution, and where if the water is still, rust patches will not form. The formation of hydrogen peroxide must be considered, therefore, incidental to and not necessary for corrosion.

It is a generally known fact that strong solutions of hydrogen peroxide will entirely protect iron from corrosion. If iron be placed in a solution of pure hydrogen peroxide, oxygen is liberated upon its surface but no rusting occurs. Moody takes this as a positive proof that oxygen alone cannot occasion corrosion. Assuming that hydrogen peroxide is a cathodic product of the action of iron on water, we would expect the presence of this reagent to inhibit the reaction, inasmuch as the law of mass action demands that the formation of a substance be limited by the concentration of that already formed.

Another possible explanation of the protective effect of hydrogen peroxide may be found in the formation of a kind of passive condition analogous to that produced by potassium dichromate, already referred to. Although much has been written upon this interesting subject there is as yet no perfectly satisfactory theory of passivity. We have noted that in the action of iron on water, when the concentration of the hydrogen ions is not sufficiently large to overcome the excess voltage of the iron surface, no action takes place unless a depolarizing substance such as dissolved oxygen is present, and then the surface divides itself into zones of different polarity. It may be possible that when iron is placed in a dichromate solution or hydrogen peroxide solution it absorbs or occludes so dense a film of oxygen upon its surface as to render the entire piece of metal so strongly cathodic that no corrosive action can take place.[1]

When bright iron is heated in the air, oxygen attacks the iron directly,

[1] A. S. Cushman, Bulletin No. 30, Office of Public Roads, U. S. Dept. of Agriculture.

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forming a closely adhering layer of oxide even if it be of but microscopic thickness. That oxygen does not unite directly with iron in aqueous rusting, is shown by the experiment already referred to with the porous cell and also by the fact that the rust formed is never adherent to the surface of the iron. The slightest rubbing with the hand produces a clean, bright surface of pure iron. Only when this layer of ferric hydroxide dries on the surface of the iron is an adherent scale produced. Moody,[1] in a very recent communication, describes an experiment in which he shows that iron does dissolve before being precipitated as rust. He uses this fact as a further proof that carbon dioxide is essential to rusting. We see ample grounds for concluding that carbon dioxide was absent in the experiments already outlined, and yet the iron surely passed into solution before precipitating.

If a piece of chemically pure iron, free from mechanical strains and without evident crystallization, be immersed in the ferroxyl indicator, the positive and negative zones will be apparent after a few moments. There appears to be an unequal concentration of oxygen or segregation of oxygen upon the surface, which cannot be explained by discernible differences in the character of the surface. If the ferroxyl indicator be removed, the surface cleaned by rubbing with a dry towel and the indicator again applied, the same separation into zones is seen, though in an entirely different configuration. The indicator is apparently a very delicate one and susceptible to changes in equilibrium, which up to the present have not been detected by other means.

Since corrosion is manifestly an electrochemical action, it seemed probable that if two specimens of iron were selected, one of which had proven itself in practice as especially resistant to corrosion, and another which had shown itself to be very susceptible to corrosion, certain differences in the electrochemical behavior should be discernible. Two sets of such specimens were obtained. The first consisted of two pieces of sheet metal which had been used as culverts in road building, one of which had given way in but a short time while the other was practically intact. The second set consisted of two strands of wire from a piece of ordinary barbed wire fencing, one of which was badly corroded upon an exposure of but six months while its neighbor was apparently in its original condition. Nothing is known of the history of the two wires; the good piece of sheet was known to be from an open hearth steel ingot containing but a trace of manganese, and in the heating and rolling of which extra precautions had been taken to prevent segregation. The poor piece was known to be from an ingot of ordinary Bessemer steel.

If corrosion be an electrochemical phenomenon depending upon the formation of an anode portion and a cathode portion and the passage of

[1] Pr. Chem. Soc. 23, 84.

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a current between these two, the rate of this corrosion may be assumed to be proportional to the difference of potential between the two surfaces. In order to determine whether there was any marked difference in the samples of iron above referred to, in regard to variation in potential between points taken at random over the surface of each, the following method was employed: In the case of the sheet metal, specimens were machined to an area of about three square inches in the form of a rectangle one inch wide by three inches in length. A block of paraffin ¼ inch thick was cut to have the same surface as the sheet metal. A number of small holes about ⅛ inch in diameter were drilled in the paraffin and the latter pressed upon the sheet after warming the same. A number of small electrically insulated cells were thus formed, the bottom of each being a definite portion of the surface of the metal. The physical condition of the different pieces of metal experimented with, was made as uniform as possible before applying the paraffin block, by polishing each upon a fine, dry sandstone. When any electrolyte, for example, hundredth-normal potassium chloride solution was placed in these cells, a difference of potential between any two could readily be measured by means of Poggendorf's compensation method. The composition of the cell was Pt-KCl-Fe-Fe-KCl-Pt. In many cases a current of sufficient intensity was set up to rapidly polarize the platinum wire electrodes which were used to complete the circuit from the electrolyte in one cell, through the measuring instrument to the electrolyte in the other cell. In order to eliminate any effect which a difference in the surface of the platinum wires might introduce, these were heated in a Bunsen burner before each measurement. By taking a measurement and then interchanging the platinum wires in the respective cells, no difference in the reading was observed, and therefore the potential found was independent of the platinum. A cell for investigating the samples of wire was made in an analogous way, using a long wooden trough in which the wires were inserted, and forming cells by building up partitions of paraffin at intervals along the length of the wire.

The differences in the average variation of any two cells taken at random over the surface of sheet metal in the one case and the two wires in the other, are very marked, a typical set of readings being shown in the following table, the figures representing differences in potential, expressed in millivolts, between various cells:

Poor Sheet.			Good Sheet.		
I	II	III	I	II	III
— 56	—60	+ 47	— 5	— 5	— 8
+ 48	+21	— 86	0	— 8	0
— 39	+30	— 48	+ 4	0	—20
— 26	—93	— 69	0	0	—20
+ 56	—31	—177	+18	— 8	0
— 30	+ 8	— 58	+ 2	+ 8	0
+ 21	+81	— 32	0	0	— 5

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Corroded Wire.			Good Wire.		
+161	+13	− 30	0	+ 2	+ 8
+ 93	−24	+ 38	+ 4	+13	0
+ 21	+13	+ 63	+13	0	+ 4
+ 43	−21	+103	0	0	+13
+ 8	−56	+ 26	+17	+ 4	+ 4
+ 30	−64	− 43	− 8	− 5	− 8
+ 55	−43	+ 47	0	+ 9	0
− 16	−52	+119	− 5	0	0
+ 78	−21	+ 8	− 8	+26	− 5

After measuring the difference of potential as above, the paraffin was in each case removed, a fresh surface obtained and the experiment repeated. No two cells ever reacted alike but there was always the marked difference between the two pieces of metal indicated above.

It is as yet too early to decide that measurements of this kind indicate the tendency of iron to corrode, but by investigating a large number of specimens of known resistance to corrosion we hope to obtain definite information on this point.

SUMMARY.

We have

(1) Proven again that carbon dioxide is not essential for the corrosion of iron;

(2) Substantiated the work of Whitney and shown that iron does dissolve in pure water in the absence of carbon dioxide and oxygen;

(3) Shown that the primary function of oxygen in the corrosion of iron is in depolarizing those cathodic portions of the iron upon which hydrogen tends to precipitate, and that a secondary function is the oxidation of the ferrous iron ion to the ferric form, with its subsequent precipitation as ferric hydroxide;

(4) Shown that the rapidity of corrosion in water is a linear function of the partial pressure of the oxygen in the atmosphere above the water;

(5) Shown that an electric current can pass between bright iron and iron covered with scale, (1) if the concentration of the hydrogen ions be increased by the presence of an acid, or (2) if oxygen or some other depolarizing substance be present;

(6) Shown that in certain instances, areas having marked difference in potential exist in far greater number upon the surface of a piece of iron prone to corrosion than upon iron which is resistant to corrosion.

This investigaton is being continued, and in a subsequent paper the more practical phases of the subject will be dealt with.

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TELLURIUM—TIN ALLOYS.

By Henry Fay.

Received June 28, 1907.

So far as the author has been able to learn, no effort has been made to make any compounds of tin and tellurium nor do any minerals containing these two elements occur in nature. The alloys of tellurium with lead[1], and with animony[2] have been described by the writer, and more recently the freezing point diagram for tellurium and bismuth has been worked out by Mönkemeyer[3].

The tin-tellurium freezing point diagram is very similar, as might be expected, to the lead-tellurium diagram. Tin and tellurium unite to form the compound, SnTe, which melts undecomposed at 769°. This compound forms a eutectic with tellurium, which contains 85 per cent. of tellurium, and a eutectic with tin of very low concentration. In the lead-tellurium series there is the compound, PbTe, forming a eutectic with tellurium containing 78.50 per cent. of tellurium. At the time the lead-tellurium series was worked upon it was supposed that the compound formed a solid solution with lead, but this view is no longer tenable, and it is now believed that lead telluride forms a eutectic of low concentration with lead. The reasons for this belief will be discussed later in the paper.

The method of work has been in all respects similar to that described in the previous papers on tellurium alloys, with the exception of the preparation of the metallic tellurium. It has been the custom in the past to recover the tellurium from the dried mud obtained from the Baltimore Copper Works by extraction with concentrated hydrochloric acid. On account of the large amount of silica present there was much difficulty not only in the extraction but in the separation of the tellurium from the gelatinous silica. Recently it has been found more expeditious and convenient to distill the selenium and tellurium from the dried mud in a current of hydrochloric acid gas. The chlorides of these two elements with traces of ferric chloride distill over and are subsequently separated by the method described by Norris, Fay and Edgerly[4]. This method involving the purification of the tellurium by means of the basic nitrate gives metallic tellurium of a high degree of purity. The whole process is very much simpler and more economical than that previously described.

The freezing points of the various alloys were determined by means of a thermo-electric pyrometer. The couple was composed of a pure platinum and a platinum ten per cent. iridium wire bound tightly together at their ends and both enclosed in thin pieces of hard glass tubing. These

[1] Fay and Gillson. Am. Ch. J., 27, 81 (1902).

[2] Fay and Ashley. Am. Ch. J., 27, 95 (1902).

[3] Z. anorg. Chem. 46, 415.

[4] Am. Ch. J. 23, 105.

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two were again surrounded by a single piece of hard glass. The junction was standardized and calibrated in the usual manner.

A number of alloys, each weighing about twenty grams were made. The tin and tellurium were both carefully weighed, placed in a porcelain crucible, and covered with a layer of powdered charcoal to prevent oxidation. The crucibles were cautiously heated until combination took place and then the heat was raised until the whole button was completely melted. The glass tubing covering the junction was warmed in the flame and then inserted into the molten alloy, which was stirred during the cooling. In those alloys containing approximately equal amounts of the two metals the heat of combination was so great in some cases as to project some of the metal out of the crucible. In these cases it was necessary to add the tellurium slowly, and in small pieces. During the cooling process readings of the galvanometer scale were made at regular intervals and these readings were subsequently plotted. The results obtained are shown in the table and are plotted diagrammatically in Fig. I.

Tin per cent.	Tellurium per cent.	Freezing points.	
.....	100	446°	
2.50	97.50	438°	399°
5.00	95.00	432°	399°
10.00	90.00	419°	399°
20.00	80.00	414°	401°
30.00	70.00	494°	399°
35.00	65.00	536°	400°
40.00	60.00	634°	399°
48.23	51.77	769°	
50.00	50.00	769°	
60.00	40.00	761°	
65.00	35.00	735°	232°
80.00	20.00	590°	232°
90.00	10.00	405°	233°
95.00	5.00	238°	232°
100.00		232°	

The curve shows one maximum point, indicating a compound corresponding to the composition represented by the formula, SnTe, and melting at 769°. This compound forms with tellurium a eutectic which melts at 399°, and which is composed of 85 per cent. of tellurium and 15 per cent. of tin. With tin, the compound also forms a eutectic, but the solubility of tin telluride in tin is so low that it was impossible to locate exactly the concentration of this eutectic. The melting point of this eutectic of low concentration would appear to be identical with the melting point of tin. This fact, however, does not seem to be an isolated case, as there are some other curves showing eutectics of extremely low concentration and correspondingly having their melting points coinciding with that of one of the constituents. In the lead-tellurium series a simi-

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lar curve was obtained and it was thought at the time that the work was done that it indicated a solid solution of lead telluride in lead. The microstructure of both series of alloys, however, would not seem to con-

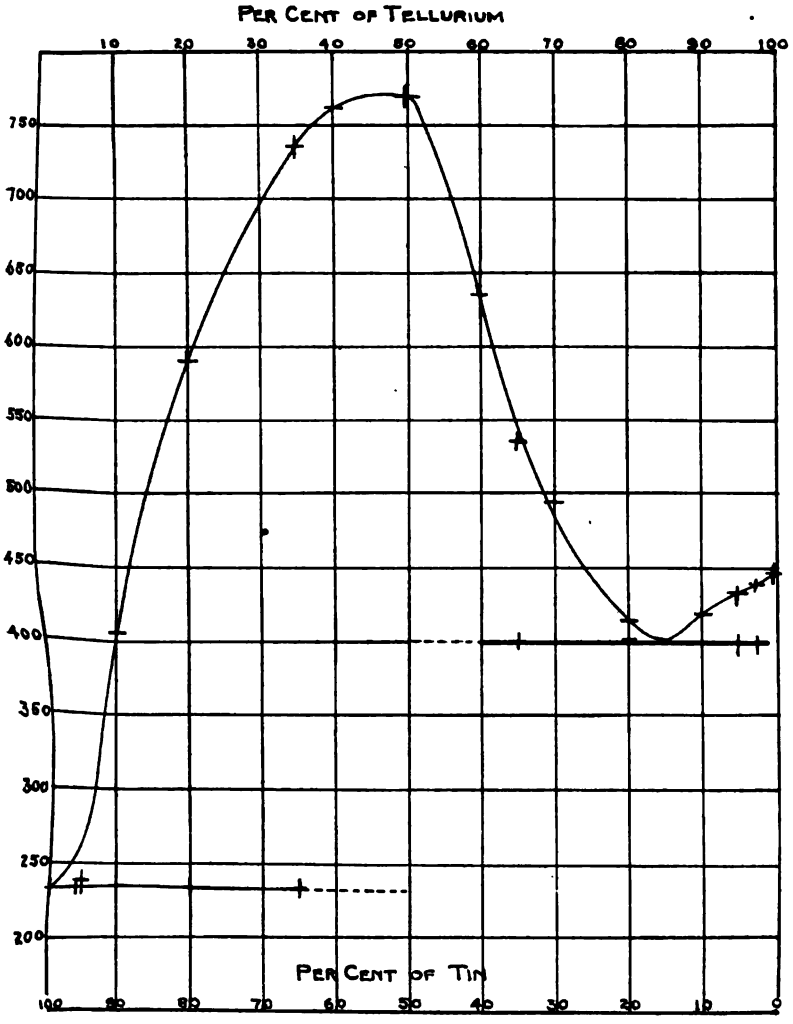


FIG. 1.

firm this belief, although it must be said on the other hand that in neither case does the eutectic structure show itself. It seems highly probable that in both cases a eutectic of low concentration actually exists. In some experiments in which buttons of definite and equal total weight with varying composition were used, the time of the separation of this eutectic was plotted and from the curve thus obtained it appeared that it

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exists in the whole field between tin and tin telluride, although the thermal effect near the tin telluride concentration was very slight. That portion of the curve lying between pure tin and tin telluride was very difficult to obtain. While only a few results are given, many other experiments were made. In many cases masses of the high melting telluride would clot together and make a good clear fusion very difficult.

The presence of the compound, SnTe, is indicated not only by the fact that the maximum point in the curve coincides with the composition demanded by the formula SnTe, but it was also identified by Tanmann's thermal method. A line drawn through the time intervals of the separation of the two eutectics ends in each case at this composition.

Furthermore the compound is clearly indicated by the micro-structure. The alloy containing 48.28 per cent. of tin shows a uniform dark field when etched with nitric acid. With increasing amounts of tellurium more and more of the eutectic shows until the composition of the pure eutectic is reached. Beyond this point crystals of tellurium are found embedded in the eutectic. The microstructure of the alloys varying from 50 to 100 per cent. of tin is very unsatisfactory, as it is only after prolonged annealing that equilibrium is reached, and there is always much oxidation during the heating.

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A STUDY OF THE CAUSES OF IMPURE NICKEL PLATE WITH SPECIAL REFERENCE TO THE IRON.

BY D. F. CALHANE AND A. L. GAMMAGE.

Received June 27, 1907.

The experiments described in the following article were performed for the purpose of ascertaining the amount of iron present in nickel plate and also to study the conditions that influence the deposition of this undesirable impurity. In the course of this work a point of considerable interest was met with and further investigated as detailed later.

It is a fact of everyday experience that nickel plate rusts on any prolonged exposure to moisture, and this rusting is pronounced to be due to small amounts of iron contained in the plate and coming from the solution during the plating process. This impurity may be conceived as constituting with the nickel a series of galvanic couples that cause rapid rusting in the presence of moisture and carbon dioxide of the air.

The universal method of plating on a commercial scale is to suspend a bar compounded of nickel and iron as anode in a bath of the double salt, nickel-ammonium sulphate, the article to be plated constituting the other pole or cathode.

The presence of the iron in the anode is due to the fact that pure nickel is not corroded rapidly enough to furnish the necessary nickel to

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the solution. Iron is the cheapest material and has a solution tension enough greater than nickel to make it effective for the end in view.

The anode bars as sold to the platers are guaranteed to be over 90 per cent. nickel. The double salt of nickel-ammonium sulphate is dissolved in hot water and diluted up to 6° to 8° Beaumé, giving a nearly saturated solution. In winter the concentration is run as low as 5° Beaumé, to prevent the salt from crystallizing out.

During the plating, as the anodes are corroded a brown sludge of basic iron salt is formed on the surface and must be brushed off every day and the accumulated deposit cleaned from the tanks weekly.

To conclusively prove the fact that iron is present in nickel plate as ordinarily deposited, a sheet of platinum was plated at a local establishment, and the deposit, about one gram, removed with hydrochloric acid and a qualitative analysis made, which showed small amounts of iron.

Attention was next turned to finding out how the iron came to be in the nickel plate. This would result either from mechanical occlusion, deposition by the current or a combination of both causes.

Portions of nickel anode bars that had been used in actual work in two different establishments were procured, and thoroughly cleaned with water and acid until only the nickel showed. Small samples of these were taken and analyses made for their iron content. Portions of four different bars were thus used. A qualitative analysis showed nickel, iron and small amounts of carbon and silicon.

The samples were analysed for iron by the basic acetate process[1] and gave 7.59 and 7.56 per cent. of iron. Two other samples were analyzed for iron by the ferric hydroxide method as is usual in commercial analysis, and gave 7.53 and 7.52 per cent. of iron. The nickel in these latter two solutions was determined by electrolysis,[2] using the customary procedure, and gave 91.96 and 92.01 per cent. of nickel. The remaining one-half per cent. was composed mainly of silicon and traces of other impurities, from which, however, no test for cobalt was obtained.

A qualitative analysis of the nickel ammonium sulphate showed as impurities traces of iron, sodium and organic matter.

A solution of the ordinary nickel salt was made up to a strength of 250 grams in three liters and this placed in each of two glass battery jars. Small pieces of the commercial anodes containing about 8 per cent. iron, were drilled and suspended by wires in the solution. Two anodes were used in each jar.

For cathodes, strips and spirals of platinum were used, so that the deposit could be stripped off. As it was observed that the shape of the

[1] Treadwell Analytical Chemistry, p. 123.

[2] Ibid., p. 112.

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cathode had some influence on the nature of the deposit, the plates and spirals were used to better study this particular point.

In the first instance, two platinum strips about 2 inches wide and 4 inches long were plated at the works of a local establishment, and on analysis of the deposit were found to contain 0.096 and 0.080 per cent. of iron. These results show a very small portion of iron, but yet enough to constitute an appreciable impurity, and account for the rusting of plated articles.

Experiments in the laboratory were directed towards the study of variations in conditions and their effect on the iron impurity. Platinum strips were used of a size about 9×4.5 cm., and which weighed about 8 grams each.

A current density of 0.04 ampère per sq. cm. was at first employed, or 2 ampères current for the total surface immersed.

In one hour a deposit of 1.940 grams was obtained. The theoretical ampère hour efficiency for nickel is 1.094 grams. This gives a current efficiency of 88.20 per cent. An analysis of the deposit for iron was made and gave 0.147 per cent. The deposit obtained in this experiment was bright, but had begun to peel, showing either a too high current density or unclean surface. The platinum was subsequently cleaned with fine sand, sodium hydroxide and hydrochloric acid or potassium cyanide.

In the next experiment two baths were run in series, with all the conditions the same in one as in the other except that one of the solutions was stirred by a rotator turning 130 revolutions per minute. The current was 0.75 ampère. An examination of the films of deposited nickel at the end of the experiment showed that each was inclined to peel and the one deposited in the solution that was stirred looked the better of the two. In one hour the plate from the solution that was not stirred had received a deposit of 0.7425 gram of nickel, showing a current efficiency of 90.48 per cent. The plate from the stirred solution had received 0.7402 gram of nickel, showing practically the same efficiency.

Here, both cathodes were stationary and one solution stirred, which had practically no effect on the current efficiency in nickel. As will be shown later, a widely different result is the case when the cathodes are rotated.

An analysis for iron in the deposits obtained in the last experiment was made and gave 0.13 per cent. for the still solution and 0.36 per cent. for the stirred solution. As will be seen from the previous figures, the agitation of the solution greatly increases the iron impurity of the nickel deposit, showing large amounts of mechanical occlusion.

The current previously used was evidently too great, and a duplicate of the experiment last described was carried out using 0.2 ampère

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current. This gave a firmly adhering deposit with practically the same amounts of iron impurity as last detailed.

In the next experiment the cathode in one case was stationary, and in the other was rotated at 130 turns per minute. The platinum sheets were used as before. The results here in one respect were surprising. After two and one-half hours' time with 0.1 ampère current, there was deposited on the stationary cathode 0.2506 gram of nickel and on the rotated one 0.0380. The still deposit was bright and firmly adherent. The other one was dark and less firm. This corresponded to an efficiency of 91 per cent. and 12 per cent. in nickel in the respective cases.

A duplicate of the above trial was made under exactly the same conditions, the current acting for two hours. The still electrode received 0.2080 gram deposit, corresponding to an efficiency of 94 per cent., and the one that was rotated, a deposit of 0.0354 gram, answering to an efficiency of 16 per cent. The deposits of the last two experiments were analyzed for iron content and gave for the still cathode 0.11 and 0.10 per cent. and for the rotating cathode 0.54 and 0.56 per cent.

With such small deposits of iron these figures agree very well. The striking deficiency of nickel deposit in the case of the rotated cathode is again to be noted.

With the same speed of rotation and a current of 0.5 ampère, a run of an hour's duration was made to see if the rotated cathode would take on more nickel with the larger current. On the still cathode the deposit was 0.4945 gram, corresponding to an efficiency of 90 per cent. The rotated cathode received a deposit of 0.0659 gram, answering to an efficiency of 12 per cent.

During the previous experiments, it was noticed that although the electrolyte when the start was made was perfectly clear, it grew slightly cloudy during the time of the experiment. This led to the idea that some of the iron impurity might be kept out of the nickel deposit by surrounding the anodes with some filtering medium. Canvas bags were made, and in these pockets each anode was hung. With this arrangement, and freshly prepared solutions of nickel salt, 0.1 ampère in three hours deposited 0.2928 gram on the still cathode, and 0.0594 gram on the cathode rotated at 260 turns per minute. This corresponds to current efficiencies of 90 per cent. and 18 per cent. respectively.

The analysis for iron gave 0.05 and 0.75 per cent. respectively. Checks on these results under the same experimental conditions gave 0.07 and 0.80 per cent. of iron respectively.

As it was found that the platinum strips would not stand a rotation higher than 260 turns per minute, spirals were used for the faster speeds. In stripping the nickel from the platinum, the deposits on the still cathodes dissolved with considerable difficulty in the hydrochloric acid,

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while the deposits from the cathodes that were rotated were in many instances dark colored and dissolved very readily, as though an oxide might be present. The bags added no appreciable resistance to the bath. An experiment was tried without the bags around the anodes, rotating one spiral as cathode at 260 turns per minute and another as cathode at 1041 turns per minute. After four and one-half hours the deposits were 0.3415 gram on the 260 speed cathode and 0.2716 gram on the 1041 speed cathode. This corresponds respectively to current efficiencies of 69 and 55 per cent. The current used was 0.1 ampère. The higher speed here appears to cut down the efficiency in a marked degree. The deposits in the two cases were analyzed for the iron present and gave 0.70 and 0.74 per cent. The marked increase in the iron impurity without the bags at this high rotation is noticeable, and also the near agreement in results from widely differing speeds.

Another experiment was tried with the bags, under the same conditions as before. In three hours, 0.2315 gram of nickel was deposited on the one rotated at 260 turns, and 0.1820 gr. on the one turning at 1041 revolutions. This corresponds to current efficiencies of 70 and 55 per cent. respectively, checking in this respect the previous figures. The deposits were good, did not peel, and the coating, on the spiral revolved at 1041 turns, was as bright and smooth as if buffed. The analyses for iron gave 0.07 and 0.08 per cent. It was found impossible to rotate the spirals faster than 1041 turns per minute, so for higher speeds a small platinum electrode, composed of small pieces of the metal welded to a thick wire, was employed.

In the next experiment one spiral rotated at 519 turns and the other electrode at 2160 turns; in this instance the electrolyte was in a platinum dish covered with isinglass. The spiral deposit was bright but the other electrode turning at the higher speed, was dark colored. In the one case at 519 turns, the deposit was 0.2135 gram, and at the 2160 speed the deposit was 0.1314 gram, corresponding to efficiencies of 65 and 40 per cent. respectively. Analyses for iron gave 0.07 per cent. in each case.

These results with the bags as the filtering media, and without them, show conclusively that at least 0.07 per cent. of iron comes by primary deposition or deionization. Further, the faster the cathodes are rotated the less the current efficiency in nickel. This was again strikingly shown by an experiment using 0.1 ampère current for three hours through three cells in series, in one of which the cathodes rotated at 260 turns, in another at 1041 turns, and in the third where a platinum strip was used as anode instead of compound nickel, the cathode was revolving at 2160 turns. The deposits were 0.2310 gram, 0.1811 gram, and

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0.1228 gram respectively, showing current efficiencies of 70 per cent., 55 per cent. and 39 per cent. in the several cases.

The idea occurred to us that the marked current deficiencies might possibly be due to sluffing or peeling off of the deposited nickel from the rotating cathode.

In the next experiment the cathodes were rotated inside porous battery jars, new, and carefully cleaned beforehand. Inside of one a platinum plate was rotated at 260 turns, and within a second, a spiral rotated at 260 turns. The current was 0.2 ampère for three hours. The deposit on the plate was 0.2200 gram, and on the spiral 0.4313 gram answering the current efficiencies of 33 and 65 per cent. respectively.

After the experiment the solutions from the cathode compartments were carefully filtered and the filters examined for nickel. Less than 0.0005 gram was detected. This result appears to preclude the possibility of any marked loss of nickel from the electrode.

Analyses for iron on the above deposits showed 0.08 and 0.07 per cent. respectively. Duplicates of the above experiment showed 0.06 and 0.07 per cent. of iron in the two cases. In another experiment, duplicating the previous ones with jars, a spiral was rotated at 1041 turns and another remained stationary, a copper voltameter was in series with the two cells to very exactly measure the current. A current of 0.1 ampère as shown by the ammeter was sent through for three hours. On the still cathode the deposit was 0.3202 gram of nickel, and on the rotated cathode the nickel weighed 0.1691 gram.

In the voltameter 0.3704 gram of copper was deposited. This gave an exact calculation for current of 0.1044 ampère. The current efficiency in nickel deposited is respectively 93.54 and 49.41 per cent. This result shows conclusively the marked decrease in current efficiency as measured by the nickel deposited due to the rotation of the cathode. This deficiency is proportional to the speed of rotation.

The analyses for iron in the deposits of the above experiment showed 0.043 per cent. in the deposit on the still cathode and 0.08 per cent. in the deposit on the rotated one. A check on the rotated cathode gave a current efficiency of 51 and 0.08 per cent. of iron.

Using the ordinary compound anode containing about 7.5 per cent. of iron, the amount of this element present in nickel plate will average about 0.10 to 0.14 per cent.

If the electrolyte is stirred or the electrodes rotated the amount of the iron impurity increases very considerably.

If the anodes are surrounded by bags or any suitable filtering medium, as has been shown in the foregoing experiments, the amount of the iron impurity is cut down about one half.

It appears that iron to the extent of 0.04 to 0.05 per cent. will appear

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in the nickel plate in spite of filtering septa, and is probably the result of primary deposition by the current.

The use of bags over the anodes seems desirable, as they do not appreciably raise the voltage, and they keep the bath much cleaner and decrease the iron impurity in the nickel deposit by about one-half.

The surprising deficiency of the nickel deposit measured in current used, when the cathode is rotated, is interesting and will be further investigated with other metals and their compounds. This deficiency has been found to depend essentially on the speed of rotation, increasing as the speed of rotation increases. Until further investigation no attempted explanation of this fact will be advanced.

The total avoidance of small amounts of iron in the nickel plate does not seem possible with the anodes at present used in technical work.

The problem of the pure nickel anode with an effective corroding electrolyte will be further investigated in this laboratory.

LABORATORY OF APPLIED ELECTRO-CHEMISTRY,
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POTASSIUM AMMONOZINCATE.

A REPRESENTATIVE OF A NEW CLASS OF COMPOUNDS.

BY EDWARD C. FRANKLIN.

Received June 25, 1907.

Following the program of developing the ammonia system of acids, bases and salts inaugurated in this laboratory, Mr. F. F. Fitzgerald[1] has succeeded in preparing an ammonia analogue of the potassium zincate which is generally[2] assumed to be formed when metallic zinc, zinc oxide or zinc hydroxide is dissolved in an aqueous solution of potassium hydroxide. He obtained this ammono salt, to which he gave the formula, $Zn(NHK)_2.2NH_3$, by the action of an ammonia solution of potassium amide on metallic zinc and on zinc amide in accordance with the equations:

$$Zn + 2KNH_2 + Am = Zn(NHK)_2.2NH_3 + H_2,$$
$$Zn(NH_2)_2 + 2KNH_2 = Zn(NHK)_2.2NH_3,$$

which are obviously analogous to the reactions whereby Comey and Jackson[3] prepared the compounds, $Zn_3O_6Na_4H_2.19H_2O$ and $(ZnO_2NaH)_2.7H_2O$, and Förster and Günther[4] the compound to which they gave the formula, $(OH)Zn(ONa).3H_2O$[5].

Unfortunately Fitzgerald's work was brought to a sudden end by the great earthquake before entirely satisfactory evidence as to the compo-

[1] This Journal, 29, 656.

[2] Abegg's Handb. anorg. Chem., 2.2, 338.

[3] Am. Ch. J., 11, 145.

[4] Z. Elektrochem., 6, 301.

[5] This latter compound, it should be noted, is probably identical with the compound, $(ZnO_2NaH)_2.7H_2O$, of Comey and Jackson, inasmuch as the two products differ in composition by half a molecule of water only.

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sition of his product had been procured. In view of the importance of establishing definitely the existence of a compound belonging to this group of the ammonia system, the writer has continued Mr. Fitzgerald's work and has succeeded in preparing a beautifully crystallized compound, the analytical data for which point sharply to the formula, $Zn(NHK)_2.2NH_3$, or $Zn(NH_2)_2.2KNH_2$, thus confirming the earlier results.

Preparation of Potassium Ammonozincate.—The pure compound has been prepared by the action of an excess of potassium amide in solution in liquid ammonia on pure, water-free, ammoniated zinc iodide in accordance with the equation:

$$ZnI_2.4NH_3 + 4KNH_2 = Zn(NHK)_2.2NH_3 + 2KI + 2NH_3.$$

The manipulative details were carried out as follows, using the form of apparatus and methods of procedure previously described[1] by the writer. Clean metallic potassium, together with a few milligrams of platinum black, were introduced into one leg of the apparatus, after which this leg was closed before the blow-pipe. Into the other leg was then introduced the zinc salt, which was melted in a current of ammonia gas to a perfectly clear, colorless liquid, after which the tube was sealed as usual. As soon as the conversion of the metallic potassium into potassium amide was complete, the solution of the latter was poured in excess into the leg containing the zinc iodide. Zinc iodide is soluble as such to a limited extent only. Addition of a small quantity of potassium amide greatly increases the solubility of the zinc salt, a behavior for which the explanation is not obvious. Increasing the amount of potassium amide finally produces a permanent, flocculent precipitate which, in the presence of an excess of the precipitant, gradually, in the course of some hours, changes into a mass of dense, colorless, well formed crystals. After washing a few times the salt is obtained pure.

Method of Analysis.—For analysis the tube containing the pure salt was separated from the remainder of the apparatus and evacuated of its gaseous contents by means of a mercury pump at laboratory temperature. The tube was weighed, delivered of its contents, evacuated and weighed again, thus giving the weight of the salt which during this process has at no time been in contact with the air or other source of contamination with water. The substance in solution in dilute hydrochloric acid is divided into aliquot parts, in one of which the nitrogen is determined by distillation with potassium hydroxide and titration of the distillate after the usual volumetric method for ammonia. In another portion of the solution the zinc is precipitated by the addition, in excess, of a measured amount of a standard solution of sodium carbonate, followed by digestion on the water-bath until the ammonia is entirely removed and the precipitation of the zinc is complete. The filtrate from the zinc carbonate is

[1] This Journal, 27, 830.

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acidified with hydrochloric acid, evaporated to dryness and ignited, thus giving a mixture of known sodium chloride content.

Analytical Data.—The following analytical results have been obtained:

Preparation I. One-fourth of 0.5962 g. of the substance gave 0.0398 g. nitrogen; another fourth gave 0.0586 g. zinc oxide.

Preparation II. One-half of 0.6858 g. of this preparation gave 0.0930 g. nitrogen; the other half gave 0.1367 g. zinc oxide and 0.2446 g. potassium chloride.

Preparation III. One-half of 0.7424 g. of the substance gave 0.1008 g. nitrogen; one-fourth of 0.7424 g. of the substance gave 0.0727 g. zinc oxide and 0.1338 g. potassium chloride.

From these results the following percentages of the respective constituents have been calculated:

	Calculated for $Zn(NHK)_2.2NH_3$	Found I.	II.	III.
N	27.04	26.7	27.1	27.1
Zn	31.44	31.5	31.9	31.4
K	37.70	——	37.5	37.7

It should be mentioned here that the discrepancies in the analytical data obtained by Fitzgerald were undoubtedly caused by the presence of water, very small quantities of which, acting hydrolytically on the ammono salt, set free ammonia and form the hydroxides of zinc and potassium.

It is of further interest in this connection to note that the writer, in his attempts to prepare, filter and wash this compound in a piece of apparatus devised for working with liquid ammonia solutions at atmospheric pressure, always obtained products which were low in ammonia and high in potassium and zinc, the results, as he believes, of his inability to exclude all traces of moisture when working with such a cold liquid as ammonia is at low pressures. The moisture probably finds its entrance past the numerous stoppers and stop-cocks used.

Properties of the Salt.—Potassium ammonozincate is but slightly soluble in liquid ammonia, but is dissolved energetically and with the evolution of much heat in dilute aqueous acids. It is also soluble in liquid ammonia solutions of ammonium salts. It is very susceptible to the action of water, which converts it into ammonia, zinc hydroxide and potassium hydroxide; even very short exposure to the action of the moisture of the air produces a superficial, sticky layer on the clean, dry crystals. It is not explosive. When heated *in vacuo*, potassium ammonozincate remains unaffected up to about 160°. As the temperature is increased the substance melts and gives off ammonia. One specimen heated to 250° for some hours until the evolution of ammonia had practically ceased, gave off 11.3 per cent. of ammonia and yielded a dark, vari-

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colored residue which gave on analysis 18.7 per cent. nitrogen, 36.8 per cent. zinc and 44.7 per cent. potassium. Another specimen heated to 300° for a considerable time lost 11.6 per cent. ammonia and gave a residue containing 18.8 per cent. nitrogen. The evolution of one and a half molecules of ammonia from $Zn(NHK)_2.2NH_3$ would require a loss of 12.3 per cent. in weight, while a compound of the composition $Zn(NHK)_2.\frac{1}{2}NH_3$, would contain 19.2 per cent. nitrogen, 35.8 per cent. zinc and 43.1 per cent. potassium. As the temperature is raised ammonia mixed with permanent gases is given off and at the same time rings of metallic potassium and zinc are deposited in the cooler end of the tube. When a third specimen was heated to 325° for many hours it lost 14.8 per cent. of its weight, apparently showing that even at this temperature all the ammonia of crystallization is not driven off. On emptying the tubes after heating these preparations to 250° and higher, the glass walls of the tubes were found to be much attacked by the melted salt, a fact which accounts for the divergent analytical results and at the same time discouraged any further attempts to obtain a definite compound by the elimination of ammonia from the compound, $Zn(NHK)_2.2NH_3$. In one experiment a tube lined with platinum was used in the hope that definite results might thus be obtained, but it was found that the melted salt also attacked this metal. It should be pointed out, however, that the results obtained point to the probable existence of a compound of the formula, $Zn(NHK)_2.\frac{1}{2}NH_3$.

Summary.

It is shown by the work described above that a potassium ammonozincate, an ammonia analogue of the hypothetical water salt, potassium zincate, is obtained in the form of a definite, well crystallized compound by the action of a liquid ammonia solution of potassium amide, first, on metallic zinc, second, on zinc amide, and third, on zinc iodide, in accordance with the following respective equations:

1. $Zn + 2KNH_2 + Am. = Zn(NHK)_2.2NH_3 + H_2$,
2. $Zn(NH_2)_2 + 2KNH_2 = Zn(NHK)_2.2NH_3$,
3. $ZnI_2.4NH_3 + 4KNH_2 = Zn(NHK)_2.2NH_3 + 2KI + Am.$

STANFORD UNIVERSITY,
California, June, 1907.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE ACTION OF HYDROCHLORIC ACID ON MANGANESE DIOXIDE.

(Preliminary Paper.)

BY WILLIS B. HOLMES.

Received June 11, 1907.

A great deal of work has been done upon the interaction of hydrochloric acid and manganese dioxide. Although the bulk of experiment-

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evidence seems to point to the probable formation of the trichloride and tetrachloride of manganese, a final decision in this case has not yet been reached. None of the intermediate products of the reaction have ever been isolated and the experimental work bearing upon this subject is of an indirect nature. Two general methods of attacking this problem have been in vogue; the treatment of manganese dioxide with an etheral solution or with an aqueous solution of hydrogen chloride and the subsequent analyses of the solutions thus obtained. The former method excludes the presence of water, except such as is formed by the reaction itself, while the latter method introduces it.

Manganese Dioxide Treated with an Ethereal Solution of Hydrogen Chloride.—Nicklès[1] treated manganese dioxide with an ethereal solution of hydrogen chloride and obtained a dark green solution, the color of which on further dilution with ether, changed to a deep violet. On saturating this solution with hydrogen chloride he obtained a green oil which he claimed contained manganese tetrachloride. One analysis gave results for

$$MnCl_4.12\ (C_2H_5)_2O.2H_2O.$$

Nicklès' results, however, are not conclusive.

Christiansen[2] suspended manganese dioxide in ether, saturated the ether with chlorine and obtained a violet solution. By decanting this violet solution he obtained a black residue[3] which also partly dissolved in ether and gave the same violet color to the solution. He then treated manganese dioxide with ether which had been saturated with hydrogen chloride and obtained a green solution. He considered that the violet solution and the green solution both contained the same dissolved substance, the difference in color being due to the presence of water in the former case. For analysis a portion of the green solution was run into a solution of potassium iodine and the liberated iodide titrated with a solution of sodium thiosulphate. From these results the available chlorine[4] was estimated. The total manganese in this solution was then determined. The average ratio of total manganese to available chlorine from seven analyses was 1 : 1.06. He thus concluded that manganese trichloride was formed in both cases. By working at a temperature of about—10° he obtained a higher ratio—approximately 1 : 1.5—and thought that the tetrachloride might be formed at lower temperatures.

Franke[5] repeated Christiansen's work and obtained the same ratio of

[1] Ann. Chem. (4), 5, 161.

[2] J. pr. Chem,, 34, 41, and 35, 57.

[3] This residue is of interest, as it probubly contained some manganese trichloride.

[4] The term, available chlorine, refers to the chlorine in excess of that required for manganous chloride.

[5] J. pr. Chem., 36, 31 and 451.

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manganese to available chlorine, approximately 1 : 1, but interpreted the results differently. He thought that hydrogen chloride, instead of water, caused the difference between the blue and green solutions; that the green solution with the excess of hydrogen chloride contained chloromanganic acid, while the violet solution contained manganese tetrachloride. Manganous chloride was always present as a decomposition product, and united with the chloromanganic acid forming manganous chloromanganate

$$MnO_2 + 6HCl \rightarrow H_2MnCl_6 + 2H_2O.$$
$$MnCl_2 + H_2MnCl_6 \rightarrow MnMnCl_6 + 2HCl.$$

The green solution on further dilution with ether separated into manganous chloride and manganese tetrachloride, the violet color becoming evident as the tetrachloride was extracted. The ratio 1 : 1 was thus interpreted. His analysis of the violet solution gave the ratio of total manganese to available chlorine from 1 : 1.68 to 1 : 2.35. This ratio indicated the presence of the tetrachloride. The violet solution treated with a little water gave a precipitate of hydrated manganese dioxide.

Manganese Dioxide Treated with an Aqueous Solution of Hydrogen Chloride.—Fisher[1] treated manganese dioxide with strong hydrochloric acid in the proportion of one part of the dioxide to ten parts of the acid. The resultant solution was filtered through spun glass and run into a burette. A known volume was then delivered into a solution of potassium iodide and the iodine titrated in the usual way. An equal volume was then run into a solution of sodium acetate and the precipitated manganese was separated, ignited and weighed as mangano manganic oxide. The filtrate was then treated with potassium iodide and the free chlorine estimated. This, subtracted from the result in the first solution, gave the available chlorine. The ratio of precipitated manganese to available chlorine was approximately 1 : 2, and hence the conclusion that the tetrachloride was formed. He assumed that the precipitated manganese was entirely a hydrated dioxide and that the tetrachloride, in the presence of hydrochloric acid, existed in a form analagous to chloroplatinic acid.

Pickering[2] repeated Fisher's work and obtained different results. His general method of procedure was the same, except that he used water instead of a solution of sodium acetate, and analyzed his precipitated manganese by a method whereby he could estimate not only the total manganese, but also the amount of dioxide which it contained. His results showed that the precipitated manganese was not entirely a dioxide but a mixture of different oxides; that the ratio of total manganese to available chlorine was nearly 1 : 1.64, and that the ratio of manganese

[1] J. Chem. Soc., 33, 409.
[2] J. Chem. Soc., 35, 654.

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dioxide to available chlorine was 1:2. He concluded that the reaction took place as follows:—

$$\text{I.} \quad 2MnO_2 + 8\,HCl \rightarrowtail Mn_2Cl_6 + Cl_2 + 4H_2O,$$
$$\text{II.} \quad Mn_2Cl_6 + 2H_2O \rightarrowtail MnO_2 + MnCl_2 + 4HCl,$$

because he was never able to obtain more than half of the manganese as a precipitate. If equation II was correct then the amount of precipitated manganese should increase if the experiment was performed in the presence of manganous chloride, whereas the amount should remain stationary if the tetrachloride was formed. The amount of precipitated manganese did increase when manganous chloride was added to the solution, which indicated the presence of the trichloride. The effect of temperature upon the amount of manganese precipitated also indicated the formation of the trichloride. If the substance was a tetrachloride, at low temperatures, 100 per cent. should be precipitated, and in the case of the trichloride only 50 per cent. At 60°, less than 10 per cent. was precipitated, and at low temperatures the amount approached 50 per cent.

Vernon[1] studied the action of hydrochloric acid on manganese dioxide by estimating, at various temperatures, the rate of evolution of chlorine. If Pickering's view is correct,

$$2MnO_2 + 8HCl \rightarrowtail Mn_2Cl_6 + Cl_2 + 4H_2O,$$

then half of the available chlorine ought to be evolved very rapidly. This was not found to be the case, especially at low temperatures. From the result of his experimental work, Vernon concluded that manganese tetrachloride is always the first product formed when manganese dioxide is dissolved in hydrochloric acid.

Wacher[2] dissolved manganese dioxide in concentrated hydrochloric acid and obtained a brown solution which, on dilution with water, gave a precipitate of hydrated manganese dioxide. He then passed chlorine into a solution of manganous chloride in concentrated hydrochloric acid, and obtained a similar brown solution. This solution also gave a precipitate of hydrated manganese dioxide when diluted with water. From these results he concluded that the tetrachloride of manganese was formed, but gave no experimental evidence to show that the precipitate was entirely hydrated manganese dioxide.

Double Salts.—Numerous double chlorides containing manganese trichloride and tetrachloride have been isolated. Rice[3] and Newman[4] obtained the double chlorides $2KCl.MnCl_3$ and $2NH_4.MnCl_3$. Meyer and Best[5] obtained similar double salts with quinoline and pyridine hydro-

[1] Phil. Mag., 81, 469, and Chem. News, 61, 203.
[2] Chem.-Ztg., 24, 285.
[3] J. Chem. Soc., 73, 258.
[4] Monatsh., 15, 489.
[5] Z. anorg. Chem., 22, 169.

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chloride $MnCl_3.2C_9H_7NHCl$ and $MnCl_3.2C_5H_5NHCl$. They also obtained the double chlorides, $2C_5Cl.MnCl_3$, $MnCl_4.2KCl$ and $MnCl_4.MnCl_3.5KCl$. Reitzenstein[1] obtained a dipyridine manganese tetrachloride.

Experimental Part.

Previous failures to isolate the intermediate products of the interaction of hydrochloric acid and manganese dioxide probably depend upon the fact that such products are decomposed by water and heat. The reaction itself liberates water, but it seemed possible by reducing the amount of water to a minimum and at the same time keeping the temperature low, to obtain some information concerning the nature of the products formed. This proved to be the case.

The method of treating manganese dioxide with a solution of hydrogen chloride in absolute ether was not found practical. While the ratio of precipitated manganese to available chlorine could be determined from such a solution, the total chlorine could not be estimated, as it was impossible to get rid of the excess of hydrogen chloride. Attempts to precipitate the product soluble in the ethereal solution by adding a large excess of carbon disulphide or toluene, proved unavailing. A green oily liquid could be obtained, but it was impossible to do anything with it. Some medium was then sought for which would not dissolve any of the compounds of manganese formed and at the same time would dissolve hydrogen chloride and not be affected by it, or by any of the decomposition products of the reaction. Carbon tetrachloride seemed to fulfill the necessary conditions and was used throughout for the preparation of material.

The following method of procedure was followed. Five grams of precipitated manganese dioxide was mixed with 200 cc. of carbon tetrachloride and put in a long necked 500 cc. vacuum flask. This flask was then inserted in a shaking machine. The shaking machine was made of a board 40 x 15 cm., with a hole in the middle for the insertion of the neck of the flask and supported at each end by a 30 cm. upright. The neck of the flask was held in place by a perforated rubber stopper. A short shank extending from the side of the board was connected with an eccentric on a wheel run by a small motor. This gave a lateral motion to the flask, which was inserted in a pneumatic trough filled with finely ground ice and water. The shaking served the double purpose of keeping the flask and its contents cold and of agitating the mixture. Dry hydrogen chloride was then bubbled through the carbon tetrachloride. As water was formed during the reaction, no extreme precautions were taken to dry the gas, although it was passed through several towers filled with beads and sulphuric acid. Hydrogen chloride is not extremely soluble in carbon tetrachloride, so the gas was allowed to bubble through

[1] Z. anorg. Chem., 18, 290.

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for an hour and a half. The reaction was then practically complete and the solid residue in the flask was separated by filtration.

The filtrate of carbon tetrachloride gave no test for manganese, but was colored yellow from the dissolved chlorine. A large amount of chlorine was always formed, and could even be detected in the wash bottle used to absorb the unused hydrogen chloride.

The solid residue consisted of a greenish black substance, which on standing slowly decomposed with the evolution of chlorine and hydrogen chloride. When it was dried in a dessicator with potassium hydroxide and sulphuric acid, decomposition set in and a substance of a reddish brown color remained; but when dried quickly by means of filter paper and warmed, it gave off chlorine and hydrogen chloride. A little put in a large amount of water gave an immediate precipitate, probably hydrated manganese dioxide. Treated with absolute ether, it gave a solution of an intense violet color. On standing, this solution gradually lost its violet color and manganous chloride separated out; but if kept cold the solution retained its color from twelve to forty-eight hours. If hydrogen chloride was passed into this violet solution, it turned green. On continued washing of the original residue with ether the compound which imparted the violet color was entirely dissolved out and a reddish brown residue remained. This substance which dissolved in ether with the formation of a violet solution proved to be manganese trichloride.

The reddish brown residue was much more stable than the original residue. It could be kept in a dessicator for a long time without undergoing any appreciable decomposition, but decomposed immediately on exposure to moist air. When warmed it gave off chlorine and left a residue of manganous chloride. It dissolved in absolute alcohol forming a solution of a deep wine color which slowly decolorized on standing. This substance proved to be manganese tetrachloride. About one-half of the original residue was manganese trichloride, the remainder being a mixture of manganous chloride and manganese tetrachloride.

Manganese Trichloride.—The analysis of this substance offered many difficulties. The solid could not be prepared in a condition pure enough for analysis. Attempts to obtain the trichloride from the ethereal solution by evaporating the ether by means of a current of dry cold air proved unavailing, as decomposition always set in. The analysis of the ethereal solution was then attempted. In preparing this solution for analysis the utmost care was necessary. It was very difficult to remove the last traces of hydrogen chloride, and all reagents used had to be anhydrous and kept at a low temperature. The work had to be performed as expeditiously as possible, and a dilute solution used in order to prevent decomposition.

The residue of mixed chlorides from the flask was first washed with

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a large amount of carbon tetrachloride. This removed part of the hydrogen chloride. It was next washed with carbon disulphide to remove the carbon tetrachloride, and then transferred to a flask containing carbon disulphide, to which a little ether had been added, and shaken. This treatment seemed to be the most effective method of removing the last traces of the hydrogen chloride, and was repeated a second time. The residue was then transferred to a funnel and washed with ether, which had been cooled with solid carbon dioxide, until about two-thirds of the trichloride had been removed. The filter paper and residue were then put in a special funnel connected with a liter filtering flask. The funnel was surrounded with a jacket so that it could be kept cold by means of ether and solid carbon dioxide. The flask held 250 cc. of ether and was placed in a mixture of ice and salt. The residue was then washed with about 100 cc. of the cold ether, and this solution, diluted with the ether in the flask, was used for analysis.

In the analysis, three quantities were estimated; the available chlorine, the total chlorine, and the total manganese. In certain cases the precipitated manganese was also obtained. A 50 cc. pipette, protected by a drying tube, was used to run off equal portions of the solution into six receptacles. The first four consisted of liter filtering flasks fitted with rubber stoppers and carrying glass tubes large enough for the insertion of the pipette. One and two each contained about 300 cc. of a dilute solution of potassium iodide, and were used to estimate the available chlorine. Three and four each contained about 300 cc. of a dilute solution of silver nitrate to which a little nitric acid had been added, and were used to estimate the total chlorine. The arms of the flasks were connected with U tubes containing the same solutions, and these in turn were connected with an aspirator. Air was aspirated through each flask during the filling. The contents of the tubes were afterwards added to the flasks. Five and six were beakers each containing about 200 cc. of water, and were used to determine the total manganese.

The iodine was titrated with a 1/10 normal solution of sodium thiosulphate, and from the results obtained the available chlorine was estimated. The silver chloride was determined by the regular crucible method and the total chlorine estimated. Only a part of the manganese was precipitated, so ammonium hydroxide and bromine water were added to the solution to precipitate all the manganese. The precipitate was then filtered, washed, ignited in a Rose crucible and weighed as mangano-manganic oxide. It was then converted into manganous sulphide and weighed again. When the quantity of manganese was very small, the oxide and sulphide methods gave identical results, but with

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larger amounts there was a slight variation. The sulphide results were used throughout as being the more reliable.

Analysis I.—This analysis was a preliminary one performed to get some idea of the ratio between the available chlorine and the total chlorine. It gave results as follows :—

Available chlorine.	Total chlorine.
0.0198 g.	0.c618 g.
0.0198 g.	

Ratio of available chlorine to total chlorine, 1 : 3.12

Analysis II.—This analysis was performed before it was realized that the manganese trichloride retained some hydrogen chloride. The results are inserted, however, as they give an indication of the amount of hydrogen chloride retained. The residue was only washed with enough carbon disulphide to insure the complete removal of the carbon tetrachloride and the ethereal solution was then prepared. This washing removed some of the hydrogen chloride, but enough remained to give an indication of the probable amount retained. Two additional portions of the ethereal solution were run into two beakers, each containing 300 cc. of water, and the filtrates were examined as follows: the first was tested for free chlorine with a negative result, and the second for manganese which had not been precipitated.

Available chlorine.	Total chlorine.	Total Manganese	Manganese in filtrate.
0.0212 g.	0.0758 g.	0.0346 g.	
0.0212 g.	0.0757 g.	0.0343 g.	0.0168 g.

0 0344 g. of manganese requires 0.0665 g. chlorine for the trichloride. Excess of chlorine 0.0093 g., equivalent to 0 0096 g. HCl. 0.1009 g. $MnCl_3$ requires 0.0228 g. HCl for the double chloride $MnCl_3HCl$. The above results suggest the double chloride $2MnCl_3.HCl$, but are indicative only and need further confirmation. The ratio of available chlorine to the calculated total chlorine is 1: 3.13.

Analysis III.—The solution for this analysis was made with all possible precautions, but was a little too concentrated and a slight decomposition was observed. Two additional portions of the ethereal solution were used to determine the ratio between the precipitated manganese and the manganese in the filtrate. These portions were each run into 500 cc. of water and immediately filtered.

Available chlorine.	Total chlorine.	Total manganese.	Precipitated manganese.	Manganese in filtrate.
0.0209 g.	0.0684 g.	0.0348 g.	0.0167 g.	0.0183 g.
0.0209 g.	0.0684 g.	0.0346 g.	0.0167 g.	0.0179 g.

Theoretical ratio, $\frac{Mn}{Cl_3} = 0.517$. Found 0.507.

0.0347 g. of manganese should require 0.0671 g. of chlorine for the trichloride.

Ratio of available chlorine to total chlorine, 1 : 3.27.

Ratio of precipitated manganese to manganese in the filtrate 1 : 1.08.

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Analysis IV.—This analysis was made to determine the ratio between the total manganese and the total chlorine. Precautions were taken to wash the residue very carefully, and use a very dilute solution to insure a minimum of decomposition.

Total chlorine.	Total manganese.
0.0319 g.	0.0164 g.
0.0320 g.	0.0165 g.

Theoretical ratio, $\frac{Mn}{Cl_2} = 0.517$. Found 0.515.

Properties of the Trichloride:—Manganese trichloride is a solid, almost black in color, with a slight greenish tinge. Heat breaks it up with the evolution of chlorine, and it is immediately decomposed by water. Absolute ether is the best solvent yet found for the trichloride. When allowed to stand in a desiccator it decomposes into manganous chloride and manganese tetrachloride. All samples thus treated gave the reddish brown substance characteristic of the tetrachloride. The trichloride dissolves in absolute alcohol, giving a wine colored solution which answered all tests for the tetrachloride. A small amount of this wine colored solution treated with a large amount of absolute ether and kept cold soon assumed the violet color characteristic of the trichloride. It is thus possible to pass from one chloride to the other and back again. This, together with the fact that only half of the manganese is precipitated when the ethereal solution is run into water indicates that the breaking down of the trichloride takes place in two stages as Pickering[1] observed.

$$\text{I.} \quad Mn_2Cl_6 \rightarrowtail MnCl_2 + MnCl_4.$$
$$\text{II.} \quad MnCl_4 + 2H_2O \rightarrowtail MnO_2 + 4HCl.$$

The composition of the precipitate has not yet been determined. This will be done, however, when the quantitative study of this reaction is taken up.

Manganese Tetrachloride.—The tetrachloride was prepared by treating manganese dioxide, suspended in carbon tetrachloride, with hydrogen chloride. The same method of procedure as was used in preparing the trichloride was followed, and the same precautions observed. The residue was washed with absolute ether to remove the trichloride. Persistent washing with ether failed to remove the last traces of the trichloride, so the residue was dried by means of filter paper and put in a desiccator to allow the remaining trichloride to decompose. This failure to remove the last traces of the trichloride was probably due to the slight decomposition of the tetrachloride when some halogen absorbent was present. Samples of the tetrachloride when first suspended in ether gave no coloration, but the ether soon assumed the violet color of the trichloride. Attempts to prepare pure manganese tetrachloride by the above method

[1] J. Chem. Soc., 35, 654.

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proved unavailing, as manganous chloride was always formed. Absolute alcohol was the only solvent found in which the tetrachloride was soluble, and such a solution was analyzed. Manganese chloride is soluble in absolute alcohol, so the amount present had also to be determined.

The solution for analysis was prepared in the following way: The residue after standing in the desiccator was transferred to the funnel of the special filtering flask previously described. The funnel was kept cold by means of ether and solid carbon dioxide. The flask held 250 cc. of absolute alcohol, and was surrounded with a mixture of ice and salt. About 100 cc. of absolute alcohol, which had been cooled with solid carbon dioxide, was then filtered through this funnel. Four portions of the resultant solution were then pipetted off, and run into the same flasks as were used with the trichloride for the estimation of available and total chlorine. Two additional portions were run into two beakers, each holding 500 cc. of water and the precipitated manganese then determined. This result gave the amount of manganese contained in the tetrachloride. The filtrate contained manganous chloride and this manganese was then precipitated and estimated. The sum of the two gave the total manganese. In the analysis one precaution had to be observed. The precipitated manganese dioxide and alcohol interact unless the precipitation is made in a large volume of water and the filtration performed immediately.

Analysis I.—In this analysis the manganese was precipitated in 300 cc. of water, and the filtration was delayed for a short time. The results consequently are a little irregular.

	Found.	Calculated.
Available chlorine	0.0192 g.	
	0.0192 g.	
Total chlorine	0.0872 g.	0.0874 g.
	0.0874 g.	0.0850 g.
Chlorine in $MnCl_4$		0.0428 g.
		0.0389 g.
Chlorine in $MnCl_2$		0.0446 g.
		0.0461 g.
Precipitated manganese	0.0164 g.	
	0.0151 g.	
Manganese in $MnCl_2$	0.0346 g.	
	0.0358 g.	
Total manganese	0.0510 g.	
	0.0509 g.	

$$\frac{\text{Available chlorine}}{\text{Total chlorine}} = \frac{0.0192}{0.0408} = 0.470$$

$$\frac{\text{Precipitated manganese}}{\text{Chlorine in } MnCl_4} = \frac{0.0157}{0.0408} = 0.385. \quad \text{Theory, } 0.387.$$

Analysis II.—In this analysis the manganese was precipitated in 500 cc. of water and the filtration performed immediately.

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	Found.	Calculated.
Available chlorine	0.0059 g.	
	0.0060 g.	
Total chlorine	0.0442 g.	0.0440 g.
	0.0442 g.	0.0443 g.
Chlorine in $MnCl_4$		0.0140 g.
		0.0140 g.
Chlorine in $MnCl_2$		0.0300 g.
		0.0303 g.
Precipitated manganese	0.0054 g.	
	0.0054 g.	
Manganese in $MnCl_2$	0.0233 g.	
	0.0235 g.	
Total manganese	0.0287 g.	
	0.0289 g.	

$$\frac{\text{Available chlorine}}{\text{Total chlorine}} = \frac{0.0060}{0.0140} = 0.429$$

$$\frac{\text{Precipitated manganese}}{\text{Chlorine in } MnCl_4} = \frac{0.0054}{0.0140} = 0.386. \qquad \text{Theory, } 0.387.$$

Properties of the Tetrachloride.—This chloride is a solid of reddish brown color, stable at ordinary temperature, if kept dry, but it quickly decomposes on exposure to moist air. Samples have been kept for several weeks in a desiccator without undergoing appreciable decomposition. But in a large amount of water the tetrachloride gives an immediate precipitate, probably hydrated manganese dioxide. Heated to 100° it gives off chlorine, and a residue of manganous chloride remains. When the tetrachloride is suspended in ether and kept cold it slowly decomposes into the trichloride, imparting the characteristic violet color to the solution. If an excess of alcohol is added to this solution, some tetrachloride is again formed. Suspended in ether with mercurous chloride it decomposes more rapidly, but all the ordinary reducing agents such as can be used in a solution nearly anhydrous cause immediate decomposition without the intermediate stage. Absolute alcohol seems to be the only solvent which will dissolve the tetrachloride without rapid decomposition. If the alcohol contains a little water the solution is decolorized more quickly.

Summary.

1. When manganese dioxide, suspended in carbon tetrachloride, is acted upon by hydrogen chloride, manganese trichloride and manganese tetrachloride are formed.

2. Manganese trichloride has been isolated and its properties described.

3. When an ethereal solution of manganese trichloride is mixed with a large volume of water only half of the manganese is precipitated.

4. Manganese tetrachloride has been isolated and its properties described.

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5. When an alcoholic solution of manganese tetrachloride is diluted with a large volume of water, all the manganese is precipitated.

6. Manganese tetrachloride is probably the first product formed when manganese dioxide and hydrochloric acid interact.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI, NO. 71.]

ON THE NON-EXISTENCE OF β-CADMIUM IODIDE.

By J. F. SNELL.

Received July 10, 1907.

Among the specific gravities determined by Bödeker and published in his monograph, "Die Beziehungen zwischen Dichte und Zusammensetzungen bei festen und liquiden Stoffen" (Leipzig, 1860), that of cadmium iodide was given as 4.576. Fullerton having obtained a much higher result in this laboratory, F. W. Clarke and E. A. Kebler[1] in 1883 (also in this laboratory) determined the densities of specimens of the salt prepared by a number of different methods. Portions prepared (a) by union of the elements in presence of water (b) by action of potassium iodide on cadmium sulphate with recrystallization from alcohol and (c) by action of hydriodic acid on cadmium carbonate (without removal of the free iodine present in the acid) gave results varying between 5.61 and 5.73 at temperatures of 10.5° to 18.2°; a slightly impure specimen prepared by heating equivalent quantities of the elements in an evacuated sealed tube gave 5.54 at 20°, a practically identical result. But portions prepared by the action of hydriodic acid on metallic cadmium and by the action of hydriodic acid on cadmium carbonate with the addition of metallic cadmium to remove the coloration due to free iodine had specific gravities of only 4.60 to 4.69 at 14.0° to 19.0°—results almost as low as Bödeker's. From these results Clarke and Kebler inferred the existence of two forms of cadmium iodide, the common or α-form and the form of low specific gravity, which they designated β-cadmium iodide. They pointed out that an extraordinary expansion is represented in the formation of cadmium iodide of sp. gr. 4.63 (mean of all measurements), either from the α-salt or from the elements, the respective molecular volumes being: β-salt 79.2, α-salt 64.8, mean of elements 64.3.

The present investigation was undertaken with the object of determining more precisely the conditions of formation of β-cadmium iodide and of studying the relation of this substance to the α-salt. The latter question presented some interest, since there was, on the one hand, the possibility of a dimorphism, similar to that of mercuric iodide and, on the other hand, a possibility of the one salt's being a polymer of the other, Hittorf's classical work on migration ratios having afforded evidence of the polymerization of cadmium iodide in aqueous and alcoholic solutions. The

[1] Am. Ch. J., 5, 235 (1883).

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results of the research have, however, been such as to convince me that the bodies of low density, obtained by Clarke and Kebler, cannot have been pure cadmium iodide.

Only two specimens of the iodide were obtained by Clarke and Kebler and of only one of these was an analysis published, though the other is described as "pure". The published analysis is not described in detail and the result (Cd, 30.40, I, 69.33, total, 99.73) is not entirely satisfactory. The theoretical composition of cadmium iodide is: Cd, 30.68 per cent., I, 69.32 per cent. Thus, while the quantity of iodine found was exactly theoretical, the quantity of cadmium was considerably less than the equivalent of the iodine—the discrepancy amounting to 0.9 per cent. of the cadmium found.

β-cadmium iodide is described by Clarke and Kebler as brownish in color and as decreasing in weight and increasing in specific gravity on heating, three successive heatings to 50° bringing the density up to 5.545, *i. e.* almost to the normal value for α-cadmium iodide. The loss of weight, which in one sample amounted to 5.5 per cent., is explained as "undoubtedly due to the formation of an oxide or oxyiodide with liberation of iodine". Yet the amount of insoluble material formed was "trifling". Now cadmium iodide (Mol. Wt. 366) in changing to cadmium oxide (Mol. Wt. 128) loses about two-thirds of its weight. A loss of 5.5 per cent. would, therefore, mean a transformation of 8.25 per cent. of the cadmium iodide into cadmium oxide with the formation of a quantity of oxide amounting to nearly three per cent. of the whole product—a portion that would hardly be described as trifling. If an insoluble oxyiodide were formed, the proportion of it in the heated product would be still greater. There remains only the possibility that a soluble oxyiodide was formed. Aside from the fact that no such compound is known, the quantity formed to correspond to a loss of iodine amounting to 5.5 per cent. of the original weight would be such that an analysis of the heated product would have readily revealed its presence. Thus, if the compound were Cd_2I_2O, 11.6 per cent. of the heated product would consist of oxyiodide and the analysis would yield 32.4 per cent. Cd instead of 30.7 per cent. and 67.2 per cent. I instead of 69.3 per cent. However, no analysis of the heated product appears to have been made.

The assignment of the formula CdI_2 to this substance appears, therefore, to have been made upon the strength of a single analysis, low in cadmium, and without an adequate examination of the properties and behavior of the substance itself.

The weakness of the evidence in favor of the existence of the β-salt not having been appreciated at the beginning of the present work, attempts to prepare the substance were at first confined to temperatures

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below 50°, since at this temperature, according to Clarke and Kebler, gradual transformation into the α-form takes place. Cadmium iodide was prepared in a number of different ways, some involving, others not involving, the use of hydriodic acid. The specific gravity determinations were made at 30°, the work having been begun in midsummer, when it was inconvenient to work at lower temperatures. The powdered samples were placed in 10 to 25 cc. specific gravity bottles, covered with toluene and freed from air-bubbles by means of a filter pump before the remainder of the toluene was poured in. From 6 to 30 g. of material was used with the 25 cc. and from 2 to 12 g. with the 10 cc. bottle. The specific gravity of the toluene used was determined by comparison with air-free water, a Sprengel-Ostwald pycnometer being used for this purpose. Products of specific gravity $30°/4°$ of 5.60 ± 0.02 were obtained by preparation from (a) cadmium sulphate and potassium iodide solutions, evaporated and extracted with alcohol (b) cadmium and iodine, digested under water (c) cadmium carbonate and hydriodic acid, decolorized by shaking with benzene (d) cadmium carbonate and hydriodic acid, decolorized by cadmium (e) cadmium oxide and hydriodic acid, decolorized by shaking with benzene. Equivalent quantities of iodine and cadmium turnings, heated in a sealed tube one hour at 200°-230°, did not react completely. The product, heated to fusion in a retort, yielded a distillate of iodine and left a button of 8 g. cadmium in the mass of 57 g. of main product, which latter had a specific gravity of 5.50, was grayish in color when powdered and left a slight insoluble residue of darker color when treated with either water or alcohol. The treatment of hydriodic acid with metallic cadmium, with evaporation at room temperature *in vacuo* or in air, yielded in one instance a product of high specific gravity, in others brownish products of slightly less than normal density, *viz.*, 5.53 and 5.36.

The work at room temperature having yielded nothing resembling β-cadmium iodide, experiments were now undertaken in which cadmium iodide was *heated* with hydriodic acid and crystallized by cooling. This procedure invariably yielded products of lower specific gravity than ordinary cadmium iodide. In some instances the density was only 0.1 or 0.2 lower than normal, in others it was as low as, or lower than, that of Clarke and Kebler's products. The products of very low specific gravity were all obtained in presence of metallic cadmium but I do not feel certain that its presence is essential. Some of them, *e. g.* preparations XXX and XXXIV presented a characteristic mossy appearance. None of the products of low specific gravity proved on analysis to be pure cadmium iodide.

These products, air-dried between filter papers, lost weight upon heating, the loss being, in general, greater the lower the specific gravity. One of them (XVII, sp. gr. 4.53), placed in a vacuum desiccator over phos-

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PRODUCTS RESEMBLING CLARKE AND KEBLER'S β-CADMIUM IODIDE.

Number	Method of Preparation	Specific Gravity 30°/5°	Loss on Heating Per Cent.	Cadmium Found Per Cent.	Iodine Equivalent of Cadmium Per Cent.	Iodine Found Per Cent.
XVII	CdI_2 (and a little $CdCO_3$) + HI + Cd	4.53	8.23	(1)27.96 (2)28.05	63.26	(1)67.77 (2)67.37
XVII*a*	XVII heated	5.61		30.56		
XXVI	CdI_2+HI (not decolorized)	5.185	2.95	29.50	66.55	(1)69.73 (2)68.72
XXX	CdI_2 + HI + Cd	3.93	(1)14.88 (2)15.12	(1)25.79 (2)26.00	58.51	(1)61.77 (2)65.52
XXX*a*	XXX heated			(1)30.70 (2)30.31		
XXX*b*	XXX washed with toluene	4.49	6.23			
XXXIV	CdI_2 + HI + Cd	4.96	(a) 2.76 (b) 2.70 (c) 2.83	(a)29.06[1] (b)29.03	65.63	(a)68.31[1] (b)68.28
XXXIV*a*	XXXIV heated	5.41				(a)69.29[1] (b)69.20
XXII	$CdCO_3$ + HI	5.42	1.06			
XXV	CdI_2 + HI	5.32	1.67			
	Theory			30.68		69.32

phorus pentoxide, lost over 8 per cent. of its weight in the first 24 hours, and the desiccator, when opened, was found to contain hydriodic acid gas. The additional losses of weight on standing another 24 hours in the desiccator and on heating to 120° were trifling. The residue was completely soluble in water. In another portion of the same preparation, which had been used in a specific gravity determination and thus washed with toluene and again air-dried, the loss under the same treatment was a little over 6 per cent. and, as before, was practically complete in 24 hours over phosphorus pentoxide *in vacuo*.

Determinations of cadmium and iodine were made in four of the products of low specific gravity, the cadmium being weighed as oxide, the iodine as silver iodide. The most important results obtained are given above in tabular form. In all cases the quantity of iodine was greater than the equivalent of the cadmium found. (As pointed out above, the same is true of Clarke and Kebler's analysis). Considerable differences were found in the iodine content of different portions of the same preparation (See especially XXVI and XXX), indicating that the preparations were not uniform. Microscopic examination showed that some of them contained dark globular masses attached to less strongly colored crystals, apparently ordinary cadmium iodide crystals, colored brown with free iodine. The mossy aspect noted in some of the specimens appears to be due to the arrangement of the cadmium iodide plates side by side with the edges vertical. The quantity of free iodine present in the preparations was found to be extremely small, one drop of N/10 thiosulphate solution sufficing to decolorize the solution of 0.3035 g. of preparation XVII. Yet free iodine could be smelled and in some cases even

[1] Duplicate analyses of one sampled portion.

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seen in bottles in which the bodies of low specific gravity had been standing for a few weeks. A determination of cadmium in the residue from the heating of one of the specimens (XVII) to 100°–120° and one of iodine in a similar residue from another specimen (XXXIV) gave: Cd, 30.56, I, 69.25, showing that the bodies are converted by heating into cadmium iodide (Theory Cd, 30.68, I, 69.32) without any appreciable formation of oxide or oxyiodide.

From these results the inference is unavoidable that these bodies of low specific gravity (which coincide in method of formation and in behavior with those of Clarke and Kebler) consist of cadmium iodide, containing more or less hydriodic acid and water, together with a trace of free iodine. Whether they are merely cadmium iodide crystals, wet with hydriodic acid solution or contain the hydrogen iodide in solid solution or in chemical combination with a part of the cadmium iodide is not clear. By cooling to $-25°$ a solution of cadmium iodide in saturated hydriodic acid, Berthelot[1] obtained crystals which he believed to comprise a compound of hydriodic acid with cadmium iodide, but this substance was dissociated at room temperature and for that reason could not be isolated. Drying on a porous plate yielded a yellowish, anhydrous(?), crystalline substance, containing 5.3 per cent. of hydriodic acid. He also noted that cadmium iodide crystals absorb an appreciable quantity of hydriodic acid gas. I think it probable that the hydrogen iodide is contained in the cadmium iodide crystals in the form of a solid solution and, retaining its affinity for water, causes the absorption of water into the crystals.

In the course of this investigation I have twice observed that, when several crops of crystals are taken from a solution containing hydriodic acid, the later crops are whiter than the earlier but become dark on long standing. From this it would appear that the cadmium iodide is capable of dissolving free iodine as well as hydrogen iodide.

Bödeker, in his specific gravity determinations, avoided the use of powders and he explicitly states that in some instances he fused his compounds in the apparatus used as a pycnometer. This suggested the possibility of the formation of a modification of cadmium iodide of low specific gravity at some temperature higher than the boiling point of hydriodic acid solution. Although my own observations and those of Clarke and Kebler with cadmium iodide prepared from the elements by heating in a sealed tube indicated the contrary, it was thought worth while to repeat Bödeker's experiment. 10 grams of the salt were fused in a porcelain crucible and poured out into a porcelain dish. Apparently, a little oxidation occurred in the process of fusion and the cooled product was silver gray in color. A portion of this in mass, covered with toluene and

[1] Compt. rend. 91, 1026 (1880); Bull. soc. chim. 35, 291 (1881).

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freed from air by pumping, gave a specific gravity of 5.335 but a powdered portion gave 5.60. There thus appears no evidence of the existence of a second solid form of cadmium iodide, even at higher temperatures.

Summary.

1. By crystallizing cadmium iodide from solutions in hydriodic acid, products of low specific gravity, in all respects similar to the so-called "β-cadmium iodide," were obtained. On analysis these were found to contain hydriodic acid and water in addition to cadmium iodide.

2. A critical examination of Clarke and Kebler's work leads to the conclusion that there is no valid evidence of the existence of a form of cadmium iodide of lower specific gravity than 5.6.

SOME REACTIONS DURING WATER TREATMENT.[1]

By Edward Bartow and J. M. Lindgren.

Received July 8, 1907.

The necessity for a treatment to improve the University of Illinois Water Supply is shown by a variety of unsatisfactory features viz: turbidity forming on exposure to the air; sediment varying in color from black to red according as the amount of oxidation of the iron salts varies; trouble from crenothrix in the mains; soft scale, clogging the feed pipes of boilers and trouble in dairying and photography. The Champaign and Urbana city water which is drawn from the same geological formation, has the same drawbacks and also causes incrustation in tea-kettles and the clogging of water backs in ranges and furnaces.

In attempting to improve the water by removing the carbonates of calcium and magnesium, the amounts removed did not correspond to our calculations. Analysis of the water had been made gravimetrically and also by the briefer methods suggested by the American Public Health Association. The results of the former analysis are as follows.

Analysis of Water from University of Illinois Water Supply.

Ions	Parts per Million	Hypothetical Combinations		Parts Per Million	Grains Per U. S. Gallon
Potassium, K	2.6	Potassium nitrate,	KNO_3	1.1	0.06
Sodium, Na	29.0	Potassium chloride,	KCl	2.9	0.17
Ammonium, NH_4	2.3	Sodium chloride,	NaCl	3.5	0.20
Magnesium, Mg,	34.9	Sodium sulphate,	Na_2SO_4	3.6	0.21
Calcium, Ca	70.1	Sodium carbonate,	Na_2CO_3	60.5	3.52
Iron, Fe	1.0	Ammonium carbonate,	$(NH_4)_2CO_3$	6.1	0.36
Aluminium, Al	1.3	Magnesium carbonate,	$MgCO_3$	121.2	7.07
Nitrate, NO_3	.7	Calcium carbonate,	$CaCO_3$	175.2	10 22
Chlorine, Cl	3.5	Iron carbonate,	$FeCO_3$	2.1	0.12
Sulphate, SO_4	2.3	Alumina,	Al_2O_3	2.5	0.15
Silica, SiO_2	18.9	Silica,	SiO_2	18.9	1.10
		Total,		397.6	23.18

[1] Read at the Toronto Meeting of the American Chemical Society.

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From the results of these analyses we calculated the amount of lime necessary to react with the acid carbonates of calcium and magnesium, and treated the water accordingly.

An analysis of the water after treatment showed that the reduction in alkalinity was less than expected. The use of varying amounts of dry water-slacked lime made apparently no change in the speed of the reaction nor in the reduction of the alkalinity. On the supposition that the reaction would be more rapid and more complete if lime water was used, varying amounts were tried but without satisfactory results.

With a view to explaining the difficulty and determining just what reactions occur on each addition of lime, (calcium hydroxide) a series of tests was planned. A liter of water was measured into each of 19 two-liter glass stoppered bottles. Varying portions of a saturated solution of lime water, 10 cc. of which were equivalent to 23 milligrams of calcium carbonate were added to each of the 19 samples. The varying amounts of lime water used, with the equivalent in terms of calcium carbonate, are shown in Table 1. Since previous experiments had shown that the reaction was practically complete at the end of six hours, the precipitate formed in each bottle was filtered off at the end of that time. In the filtrate the alkalinity to phenolphthalein and methyl orange and the content of magnesium and calcium were determined. The results of these determinations are shown in Table 1 and a diagrammatic representation is given on Plate 1.

TABLE 1

TREATMENT OF THE UNIVERSITY OF ILLINOIS WATER SUPPLY WITH LIME

No.	Lime Water cc.	Amount of Lime Used Milligrams as $CaCO_3$	Alkalinity to Phenolphthalein: Filtrate Parts per million	Alkalinity to Phenolphthalein: Cor. for volume Parts per million	Alkalinity to Methyl Orange: Filtrate Parts per million	Alkalinity to Methyl Orange: Cor. for volume Parts per million	Calcium: CaO in 250 cc. Milligrams	Calcium: $CaCO_3$ Cor. for volume Parts per million	Magnesium: $Mg_2P_2O_7$ from 200 cc. Milligrs.	Magnesium as $MgCO_3$ Cor. for volume Parts per million
1	0	0	0	0	387.5	387.5	26.5	188.7	33.1	124.4
2	10	23	11.5	11.7	378.0	381.8	27.5	198.6	33.2	126.0
3	20	46	10.5	10.7	354.9	361.9	25.8	187.5	33.8	118.0
4	40	92	16.8	17.5	312.9	325.4	18.0	133.9	36.0	131.6
5	60	138	18.9	20.1	270.9	287.1	12.9	97.4	40.5	126.0
6	70	161	12.6	13.5	256.2	274.1	10.8	82.3	39.4	126.0
7	80	184	12.6	13.6	241.5	260.8	9.0	69.0	37.3	121.6
8	100	230	18.9	20.8	222.6	244.9	7.1	54.9	34.2	113.6
9	120	276	31.5	35.3	212.1	237.6	6.6	52.6	34.5	116.0
10	140	322	42.0	47.9	203.7	232.2	5.3	43.2	32.7	112.0
11	160	368	52.5	60.9	200.5	232.6	5.7	46.2	31.9	110.8
12	170	391	65.1	76.2	193.2	226.0	5.7	46.7	30.4	105.2
13	180	414	66.3	78.2	184.8	218.1	5.7	48.4	27.8	99.6
14	200	460	65.1	78.1	163.8	196.6	5.5	46.7	23.4	84.4
15	220	506	58.8	71.7	138.6	169.1	5.1	43.9	5.3	19.2
16	240	552	58.8	72.9	111.3	138.0	4.5	39.7	5.2	19.2
17	260	598	52.5	63.3	98.7	124.4	4.4	38.9	7.7	27.6
18	280	644	50.4	64.5	98.7	126.3	7.0	63.9	5.0	19.2
19	300	690	48.3	62.8	94.5	122.8	6.3	58.4	4.8	19.2

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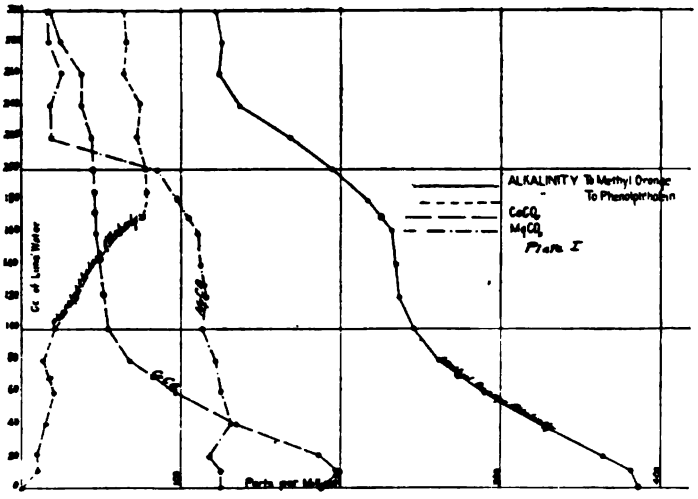


PLATE I.—Water Containing Bicarbonates of Alkalies and Alkaline Earths Treated With Lime.

The reactions with a water of this class apparently take place in four stages. During the first stage, the reaction is between the calcium hydroxide and the free carbon dioxide, during which the alkalinity to phenolphthalein remains negative, the alkalinity to methyl orange and the calcium content increases, and the magnesium content is unaffected.

During the second stage, the calcium hydroxide reacts with the calcium acid carbonate. The calcium content and the alkalinity to methyl orange decrease at equal rates; the magnesium content and the alkalinity to phenolphthalein are practically constant.

During the third stage, the calcium hydroxide reacts with the sodium bicarbonate, the alkalinity to methyl orange is unchanged, the alkalinity to phenolphthalein is increased, while the content of calcium and magnesium are constant.

During the fourth stage, the calcium hydroxide reacts with the magnesium bicarbonate with the formation of magnesium hydroxide and calcium carbonate accompanied by a decrease of the alkalinity to both methyl orange and phenolphthalein and decrease in the content of magnesium.

A fifth stage might be noted when an excess of calcium hydroxide has been added. The calcium, and the alkalinity to both methyl orange and phenolphthalein increase.

The formulas illustrating the reactions during the various stages are as follows :

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1. $Ca(OH)_2 + 2CO_2 = CaCO_3H_2CO_3$.
2. $Ca(OH)_2 + CaCO_3H_2CO_3 = 2CaCO_3 + 2H_2O$.
3. $Ca(OH)_2 + 2NaHCO_3 = CaCO_3 + Na_2CO_3$.
4. $2Ca(OH)_2 + MgCO_3H_2CO_3 = 2CaCO_3 + Mg(OH)_2 + 2H_2O$.

Under the conditions of the experiment we would not wish to imply that these reactions take place in entirely the order named. There is evidently some overlapping, but the diagrammatic representation shows that the principal part of the reactions takes place in this order.

In order to confirm our results a second water was chosen from the well of the Illinois Hotel Company, at Bloomington, Illinois. An analysis of this water is as follows:

ANALYSIS OF WATER FROM ILLINOIS HOTEL CO., BLOOMINGTON, ILL.

Ions	Parts Per Million	Hypothetical Combinations		Parts Per Million	Grains Per Gallon
Potassium, K	4.9	Potassium nitrate,	KNO_3	0.6	0.03
Sodium, Na	84 4	Potassium chloride,	KCl	9.0	0.52
Ammonium, NH_4	10.8	Sodium chloride,	NaCl	15.2	0.89
Magnesium, Mg	30.1	Sodium sulphate,	Na_2SO_4	4.4	0.26
Calcium, Ca	55.9	Sodium carbonate,	Na_2CO_3	177.2	10.33
Iron, Fe	6.6	Ammonium carbonate,	$(NH_4)_2CO_3$	28.7	1.67
Alumina, Al_2O_3	1.4	Magnesium carbonate	$MgCO_3$	104.2	6.07
Nitrite, NO_3	0.4	Calcium carbonate,	$CaCO_3$	139.5	8.13
Chlorine, Cl	13.5	Iron carbonate,	$FeCO_3$	13.7	0.80
Sulphate, SO_4	3.0	Alumina,	Al_2O_3	1.4	0.08
Silica, SiO_2	17.7	Silica,	SiO_2	17.7	1.03
Bases	.6	Bases,	——	0.6	0.03
		Total		512.2	29.84

This is shown to contain a larger proportion of sodium bicarbonate, but smaller amounts of the bicarbonates of calcium and magnesium. The other constituents are about the same as in the University of Illinois water supply.

Portions of this water were treated with lime water as in the previous experiment. The results of the treatment are shown in Table 2 and represented diagrammatically on Plate 2. It will be noted that the methyl orange alkalinity curve corresponding to the reaction between calcium hydroxide and calcium bicarbonate is shorter. The line denoting the reaction between calcium hydroxide and sodium bicarbonate is longer, while the curve where magnesium is reacted upon is shorter, indicating the truth of our hypothesis as to the order of reaction.

Precipitation with Sodium Hydroxide.—A series of tests using sodium hydroxide instead of calcium hydroxide was next carried on. The University water supply was treated. The analytical results are shown in Table 3 and a diagrammatic representation is seen on Plate 3.

Comparing Plates 1 and 3 it will be noted that the stages of the re-

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actions with sodium hydroxide correspond to those with lime. The first stage, indicated by the increase in alkalinity to methyl orange and the very slight decrease in the amount of calcium, shows reaction between the sodium hydroxide and free carbon dioxide. The second stage, indicated by the decrease in the calcium content and of the alkalinity to methyl orange, shows the reaction taking place between the sodium hydroxide and calcium bicarbonate. It will be noted that the calcium bicarbonate is removed with one-half the equivalent of sodium hydroxide. The third stage, indicated by a constant amount of calcium and magnesium implies a reaction between the sodium bicarbonate and sodium hydroxide. The fourth stage, indicated by a reduction of magnesium shows a reaction between the magnesium bicarbonate and sodium hydroxide. Here it is noted that the magnesium decreases much more slowly than when calcium hydroxide is used, and does not reach a minimum until a larger amount of sodium hydroxide has been added. The reactions during the different stages may be written as follows:

1. $2NaOH + 2CO_2 = 2NaHCO_3$.
2. $(A) 2NaOH + CaCO_3H_2CO_3 = Na_2CO_3 + CaCO_3$.
2. $(B) Na_2CO_3 + CaCO_3H_2CO_3 = CaCO_3 + 2NaHCO_3 + 2H_2O$.
3. $NaOH + NaHCO_3 = Na_2CO_3 + H_2O$.
4. $4NaOH + MgCO_3H_2CO_3 = Mg(OH)_2 + 2Na_2CO_3 + 2H_2O$.

TABLE 2.

TREATMENT OF WATER FROM DEEP WELL OF ILLINOIS HOTEL CO., BLOOMINGTON, ILLINOIS, WITH LIME

No.	Lime Water cubic centimetres	Amount of Lime Used Milligrams as $CaCO_3$.	Alkalinity to Phenolphthalein Filtrate parts per million	Alkalinity to Phenolphthalein Cor. for volume parts per million	Alkalinity to Methyl Orange Filtrate parts per million	Alkalinity to Methyl Orange Cor. for volume parts per million	Calcium CaO in 200 cc. Milligrams	Calcium $CaCO_3$ Cor. for volume Parts per million	Magnesium $Mg_2P_2O_7$ from 200 cc. milligrs.	Magnesium as $MgCO_3$ Cor. for volume parts per million
1	0	0	0	0	423	423	13.2	118.1	27.5	104.2
2	5	44	25	26	378	386				
3	10	88	38	39	343	357				
4	15	132	52	56	309	327	5.5	49.9	24.4	93.8
5	20	176	48	52	287	310				
6	30	264	69	78	261	292	3.4	33.9	20.1	85.2
7	35	308	90	103	256	292				
8	40	352	122	141	254	295	3.0	30.9	18.8	82.4
9	45	396	118	139	245	290				
10	50	440	108	129	239	287	3.0	31.9	14.9	67.2
11	60	528	109	135	192	237	2.2	24.2	6.2	29.1
12	65	572	118	148	179	225				
13	70	616	104	133	162	207	—	—	2.4	14.5
14	75	660	124	161	162	210				
15	80	704	147	194	178	236				
16	85	748	166	222	194	259	7.8	92.	1.8	9.0
17	90	792	178	243	202	274				
18	100	880	242	338	267	373				

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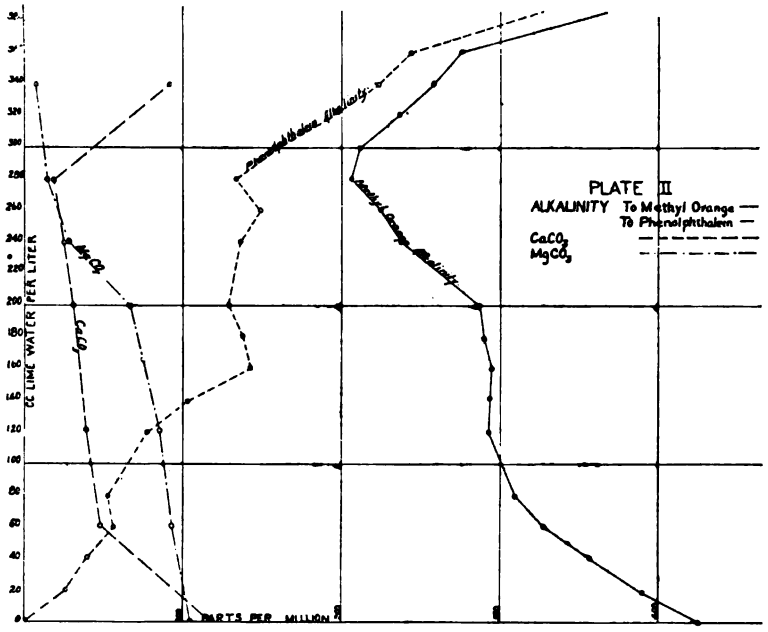


PLATE II.—Water Containing Bicarbonates of Alkalies and Alkaline Earths Treated With Lime.

TABLE 3

TREATMENT OF THE UNIVERSITY OF ILLINOIS WATER SUPPLY WITH SODIUM HYDROXIDE.

					Calcium		Magnesium	
No.	Sodium Hydroxide Solution cc.	Amount of Sodium Hydroxide Used milligrams	Alkalinity to Phenol-phthalein parts per million	Alkalinity to Methyl Orange parts per million	CaO in 250 cc. milligrs.	$CaCO_3$ Cor. for volume parts per million	$Mg_2P_2O_7$ from 250 cc. milligrams	$MgCO_3$ Corrected for Volume parts per million
1	0	0	0	386	26.5	189.1	39.7	120.5
2	1	17	0	405	26.0	185.5	39.8	120.5
3	2	34	22	403	22.1	157.8	38.3	118.8
4	4	68	26	388	12.8	91.3	38.1	118.4
5	6	102	50	388	7.2	50.4	37.4	113.2
6	7	119	72	406				
7	8	136	90	426	5.4	38.4	36.1	109.4
8	10	170	139	468				
9	12	204	147	511				
10	14	238	198	555				
11	16	272	248	589				
12	17	299	270	609	5.4	38.4	28.5	86.2
13	18	316	266	622	4.5	32.0	25.3	76.5
14	20	340	307	650				
15	22	374	334	673	3.0	21.2	15.8	47.8
16	24	408	369	702				
17	26	442	393	728	2.9	20.5	6.8	20.4
8	28	476	417	780				
9	30	510	463	813	2.1	15.0	3.2	9.7
0	32	544	518	845				
1	34	578	549	893	.8	5.5	2.2	6.6

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PLATE III.—Water Containing Bicarbonates of Alkalies and Alkaline Earths Treated with Caustic Soda.

In order to try the effect of treatment of a water containing no sodium bicarbonate, the water from a shallow well in Champaign, Illinois, was chosen for experiment.

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Analysis showed the following mineral content:

ANALYSIS OF SHALLOW WELL OF DEAN-BODE MFG. CO. CHAMPAIGN, ILL.

Ions	parts per million	Hypothetical Combinations		parts per million	grains per gallon
Sodium, Na	33.4	Sodium nitrate,	$NaNO_3$	1.6	0.09
Magnesium, Mg	50.0	Sodium chloride,	NaCl	39.6	2.31
Calcium, Ca	106.9	Sodium sulphate,	Na_2SO_4	53.7	3.13
Oxides of Iron and Alumina,	2.2	Magnesium sulphate,	$MgSO_4$	145.7	8.49
Nitrate, NO_3	1.2	Magnesium carbonate,	$MgCO_3$	36.4	2.12
Chloride, Cl	24.0	Calcium carbonate,	$CaCO_3$	266.8	15.56
Sulphate, SO_4	152.5	Oxides of iron and alumina	$Fe_2O_3+Al_2O_3$	2.2	0.13
Silica, SiO_2	11.0	Silica,	SiO_2	11.0	0.64
Bases,	3.0	Bases, with silica	———	3.0	0.17
		Total Mineral Matter,	———	560.	32.64

Portions of this water were treated with lime as in the preceding experiments. The results of the analysis of the water after treatment including determination of incrustants according to method of the Am. Pub. Health Ass'n, are shown in Table 4 and a diagrammatic representation is shown on Plate 4. The reactions in this case are also in stages. The first and second correspond to the first and second stages of the preceding experiments. During the third stage no change is evident. Further data is necessary for explanation. The fourth stage shows a removal of the magnesium bicarbonate, with a corresponding decrease of alkalinity to methyl orange and phenolphthalein. The final stage where calcium hydroxide was added in excess, shows increase of the calcium

TABLE 4

TREATMENT OF WATER FROM SHALLOW WELL, CHAMPAIGN, ILLINOIS, WITH LIME.

No.	Lime Water Used cc.	Am't of Lime Used milligrams	Alkalinity to Phenolphthalein. Filtrate parts per million	Alkalinity to Phenolphthalein. Cor. for volume parts per million	Alkalinity to Methyl Orange. Filtrate parts per million	Alkalinity to Methyl Orange. Cor. for volume parts per million	Calcium. CaO in 250 cc. milligrams	Calcium. $CaCO_3$ Cor for volume parts per million	Magnesium. $Mg_2P_2O_7$ from 200 cc. milligrams	Magnesium as $MgCO_3$ Cor. for volume parts per million	Incrustants as $CaCO_3$ parts per million
1	0	0	0	0	332	332	37.4	266.4	173.1	103.9	57.1
2	20	41	0	0	345	351	42.3	307.7	174.5		56.5
3	40	82	0	0	279	290					
4	60	124	0	0	236	255	24.0	181.6	174.5	91.7	53.6
5	80	165	0	0	209	228					
6	100	206	0	0	191	214					
7	120	247	6.4	7.4	169	191	14.4	114.8	93.0	48.8	164.8
8	140	288	11.9	13.6	118	137	8.5	68.8	157.9	94.6	45.6
9	160	330	25.7	31.0	110	129	8.6	70.8	148.2	85.4	42.2
10	180	371	29.4	35.	108	128	10.4	86.8	146.8	102.0	41.3
11	200	412	25.7	31.	94	118	11.1	93.8	137.1	104.0	38.1
12	220	453	18.3	22.	53	64	9.5	82.8	90.0	89.8	24.1
13	240	494	16.5	20.	51	64					
14	260	536	23.0	29.	39	48	11.3	99.6	63.6	95.0	15.8
15	280	577	31.2	40.	42	54					
16	300	618	41.	54.	66	86					
17	320	659	62.4	85.	83	104					
18	340	700	82.6	110.	101	133	29.62	82.5	5.5	91.2	1.3

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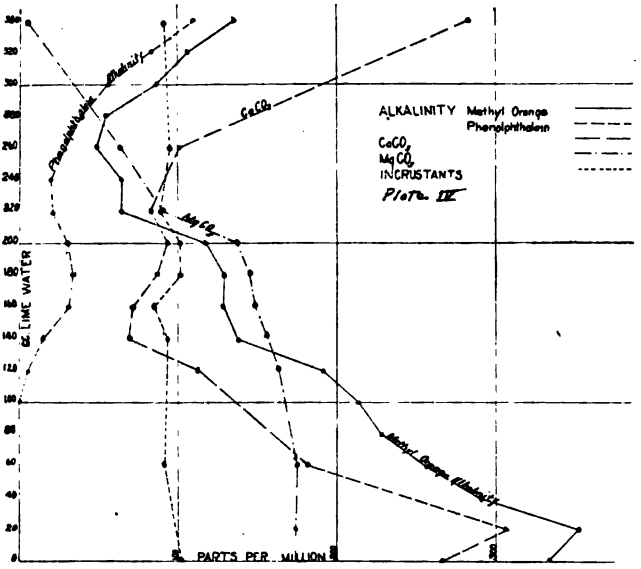


PLATE IV.—Water Containing Bicarbonates and Sulphates of Alkaline Earths Treated with Lime.

carbonate and alkalinity to both methyl orange and phenolphthalein. In this series of tests there was present in the original water 103 parts per million of sulphates of calcium or magnesium. According to the method of making hypothetical combinations which has been used in this laboratory, this would be considered magnesium sulphate. The amount of sulphates (see incrustants Plate 4) of the alkaline earths are unchanged by treatment with lime. There is here a possible confirmation of the statement that the sulphate exists as magnesium sulphate, since during the third stage there is not sufficient calcium present in the water to combine with all of the sulphates present, and when the magnesium becomes insufficient to combine with all of the sulphates, the calcium content increases. We may therefore consider that a reaction takes place between magnesium sulphate and calcium hydroxide, forming magnesium hydroxide and calcium sulphate. Our data is as yet insufficient to show whether an intermediate reaction takes place between magnesium hydroxide and magnesium acid carbonate, or whether there is interference by other salts. The work of Stillman and Cox[1] would suggest the latter explanation. The series of tests indicates that lime alone is insufficient for the treatment of such water.

Before undertaking the combined treatment with lime and sodium carbonate a similar series of tests was carried on, using varying amounts of

[1] This Journal 25, 732.

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sodium carbonate. The results of these tests are shown in Table 5 and a diagrammatic representation is given on Plate 5. This series shows that the reactions take place in three stages. First, the reaction is between sodium carbonate and free carbon dioxide, with an increase in the alkalinity to methyl orange. Second, calcium bicarbonate is precipitated as calcium carbonate and incrustants are removed. Third, there is denoted an excess of reagent. The alkalinity to phenolphthalein and the alkalinity to methyl orange increase rapidly. The magnesium carbonate content remains constant throughout the whole series. The reactions of the first two stages are as follows:

1. $Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$.
2. (a) $Na_2CO_3 + CaH_2(CO_3)_2 = CaCO_3 + 2NaHCO_3$.
 (b) $2NaHCO_3 + MgSO_4 = MgH_2(CO_3)_2 + Na_2SO_4$.

In the next series of tests sufficient sodium carbonate was added to each liter of water to react with the alkaline earth sulphates present. Varying amounts of lime were then added. The analytical results are shown in Table 6 and the diagrammatic representation on Plate 6. The reactions take place in four stages. First, by sodium carbonate the neutralization of the carbon dioxide. Second, the reactions with the alkaline earth sulphates and part of the calcium bicarbonate. Third, the removal of more

TABLE 5

TREATMENT OF WATER FROM SHALLOW WELL AT CHAMPAIGN, ILLINOIS, WITH SODIUM CARBONATE.

No.	Sodium Carbonate Solution cc.	Am't of Sodium Carbonate Used milligrams as $CaCO_3$	Alkalinity to Phenolphthalein Filtrate parts per million	Alkalinity to Phenolphthalein Cor. for volume parts per million	Alkalinity to Methyl Orange Filtrate parts per million	Alkalinity to Methyl Orange Cor. for volume parts per million	Calcium CaO in 250 cc. milligrams	Calcium $CaCO_3$ cor. for volume parts per million	Magnesium $Mg_2P_2O_7$ from 250 cc. milligrams	Magnesium as $MgCO_3$ cor. for volume parts per million	Incrustants as $CaCO_3$ parts per million
1	0	0	0	0	334	334	36.1	257.6	57.3	173.2	103.9
2	20	22	0	0	369	376	39.4	260.4	56.6	174.3	101.0
3	40	44	0	0	391	404					59
4	60	66	0	0	380	402	28.1	212.4	53.3	170.4	16
5	80	88	0	0	380	411	25.7	186.8	51.8	169.0	
6	100	110	0	0	376	415	16.1	135.6	51.0	170.4	—67
7	120	132	0	0	380	426	14.4	114.8	51.0	173.2	—91
8	140	154	18	20	374	428	7.8	64.0	50.2	173.2	
9	160	176	11	13	404	468					—206
10	180	198	29	33	417	492	6.7	52.8	45.5	162.1	—221
11	200	220	35	42	437	525					—208
12	220	242	53	64	457	558	4.9	42.8	45.5	167.6	—279
13	240	264	59	72	481	597					—358
14	260	286	55	70	503	633	3.2	28.8	——	——	—426
15	280	308	57	73	525	672					—411
16	300	330	61	83	556	722	3.9	34.0	43.1	169.	—475
17	320	352	81	106	569	751					—620
18	340	374	92	121	590	789	3.4	31.6	42.3	170.4	—561

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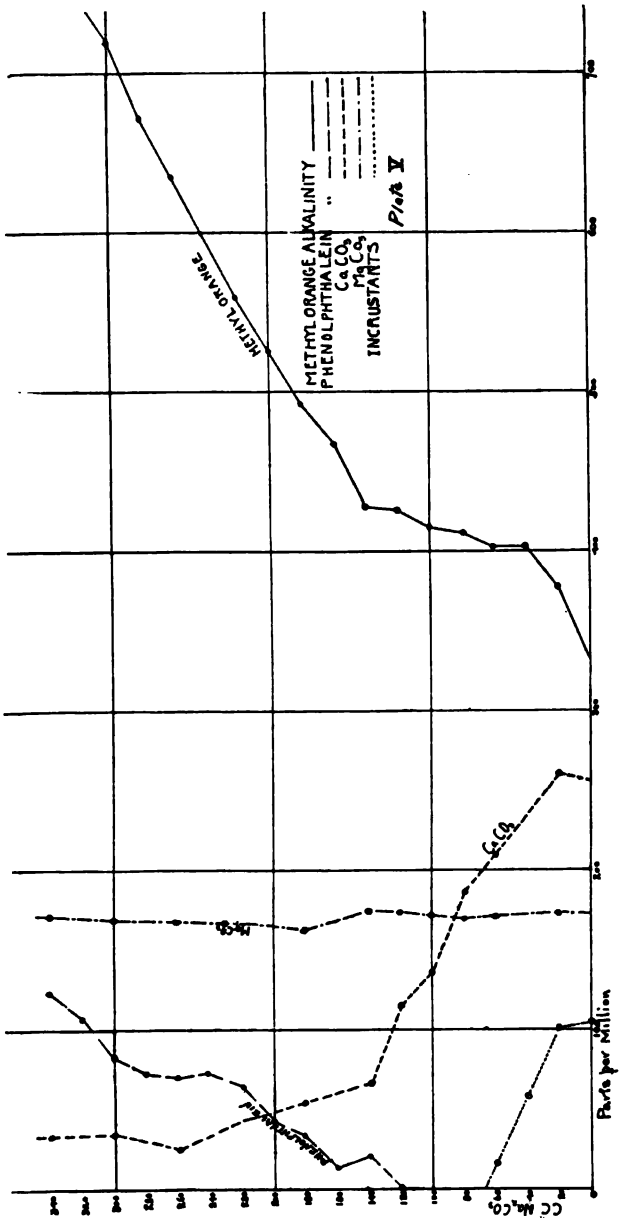


PLATE 5.—Water Containing Bicarbonates and Sulphates of Alkaline Earths Treated With Soda Ash.

calcium bicarbonate. Fourth, reaction between magnesium bicarbonate and calcium hydroxide, with removal of magnesium bicarbonate. The reactions during the various stages are as follows:

1. $Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$.
2. (a) $Na_2CO_3 + CaCO_3H_2CO_3 = CaCO_3 + 2NaHCO_3$.

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(b) $2NaHCO_3 + MgSO_4 = MgCO_3H_2CO_3 + Na_2SO_4$.

3. $Ca(OH)_2 + CaCO_3H_2CO_3 = 2CaCO_3 + 2H_2O$.

3. $2Ca(OH)_2 + MgCO_3H_2CO_3 = Mg(OH)_2 + 2CaCO_3$.

Conclusion.

A general comparison of the results would indicate that reactions in water treatment take place in regular order depending on the amount of reagent used.

A practical application of these results may be found useful in determining the advisability of partial or complete treatment, in the latter case adding a considerable excess of the reagent in order to remove as completely as possible incrusting constituents.

During the first and second stages of treatment with lime there is removed from 70 to 80 per cent. (see Tables) of the carbonates of calcium or about 50 per cent. of the alkaline earth carbonates. To remove only a small percentage more requires nearly double the amount of lime; and to obtain the maximum removal (about 80 per cent. in these waters) would require nearly three times as much lime.

The presence of sodium bicarbonate must be considered in water treatment. It is also probable that other salts than the acid carbonate of sodium interfere with the reactions.

Neither lime or sodium carbonate alone will give a maximum removal of incrusting constituents in waters containing sulphates. If either is to be used alone, sodium carbonate is the better.

TABLE 6.

TREATMENT OF WATER FROM SHALLOW WELL, CHAMPAIGN, ILLINOIS, WITH A CONSTANT AMOUNT OF SODIUM CARBONATE, AND VARYING AMOUNTS OF LIME.

No.	Lime Water Used cc.	Am't of Lime Used milligrams	Alkalinity to Phenolphthalein Filtrate parts per million	Alkalinity to Phenolphthalein Cor. for volume parts per million	Alkalinity to Methyl Orange Filtrate parts per million	Alkalinity to Methyl Orange Cor. for volume parts per million	Calcium CaO in 200 cc milligrams	Calcium $CaCO_3$ cor. for volume parts per million	Magnesium $Mg_2P_2O_7$ from 200 cc. milligrams	Magnesium as $MgCO_3$ cor. for volume parts per million	Incrustants as $CaCO_3$ parts per million
1	0	0	0	0	334	334	29.9	266.4	45.7	173.1	103.9
2	20	36	0	0	340	347	18.0	200.0	43.2	165.0	—5.7
3	40	72	0	0	312	324	14.4	133.5	32.7	167.5	—5.8
4	60	108	0	0	279	296	11.2	106.0	41.3	164.0	0
5	80	144	0	0	257	278	9.8	95.0	41.1	168.	—19.
6	100	180	0	0	242	266	8.1	79.5	38.0	157.5	—13.2
7	120	216	0	0	224	251					
8	140	252	20	23	211	241	7.1	72.5	37.0	159.5	18.2
9	160	288	29	34	211	245					
10	180	324	62	79	200	236	6.9	72.5	34.3	154.0	9.4
11	200	360	44	53	185	222					
12	220	396	33	40	158	192	5.2	46.0	29.8	137.0	—6.8
13	240	432	26	32	126	156	5.3	47.0	29.8	138.5	—6.9
14	260	468	28	35	110	139	6.4	57.0	15.9	75.0	—7.0
15	280	504	9	11.5	66	84	4.9	53.5	5.2	24.0	—18.0
16	300	540	11	14	70	91					
17	320	576	18	24	70	92	5.4	64.5	6.0	29.5	—15.8

Note.—To each portion of water 11 cc of sodium carbonate solution containing 116.6 milligrams Na_2CO_3 was added.

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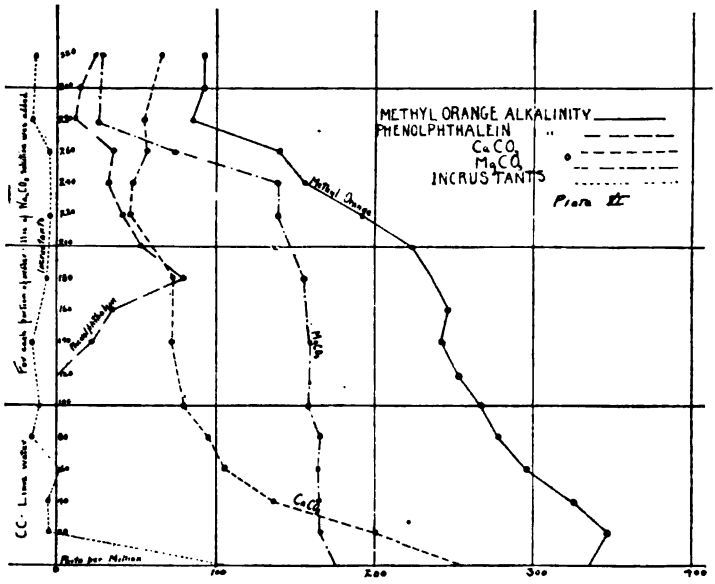


PLATE VI.—Water Containing Bicarbonates and Sulphates of Alkaline Earths Treated With Soda Ash and Lime.

ON THE OXIDATION OF HYDRAZINE. I.

BY A. W. BROWNE AND F. F. SHETTERLY.

Received July 10, 1907.

In 1902 Tanatar[1] showed that hydronitric acid could be obtained by treating a molecular mixture of hydrazine sulphate and hydroxylamine chloride in acid solution with certain oxidizing agents. Three years later it was demonstrated in this laboratory[2] that the acid could be prepared by the action of hydrogen peroxide upon hydrazine sulphate in the presence of free sulphuric acid. Still later it was found[3] that by the action of several other oxidizing agents, respectively, upon hydrazine sulphate in acid solution, varying amounts of hydronitric acid could be produced. In the present article is described a series of experiments performed for the purpose of ascertaining the conditions under which hydronitric acid is formed by the action of ammonium metavanadate in acid solution upon hydrazine sulphate.

Examination of Materials Employed.—In order to test the purity of the hydrazine sulphate (obtained from Kahlbaum, Berlin) used in these experiments, the percentage of sulphur was determined in six different samples of the material. Found: 24.57, 24.60, 24.56, 24.59, 24.58 and 24.54 per cent.; theory, 24.64 per cent.

[1] Ber. 35, 1810-1811.
[2] Browne, This Journal 27, 551-555 (1905).
[3] Browne, Science (N. S.) 22, 81 (1905).

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In the ammonium metavanadate (obtained fromE. Merck, Darmstadt) the percentage of vanadium was determined by weighing the pentoxide formed by ignition of a weighed quantity of the original material. Found: 43.23, 43.18, 43.19 and 43.17 per cent.; theory, 43.67 per cent. The percentage of nitrogen was determined by distilling the ammonia liberated from a weighed amount of the material in alkaline solution into a measured excess of standard hydrochloric acid. Found: 11.84 and 11.85 per cent.; theory, 11.95 per cent.

Preparation of Solutions.—Two solutions of hydrazine sulphate were employed: one containing 15 g. of the salt per liter, and the other 10 g. The solution of ammonium metavanadate was prepared in each case by dissolving the proper amount of the salt in a certain measured amount of pure concentrated sulphuric acid and diluting with a measured amount of water after the solution had been cooled to room temperature.

General Procedure Followed in the Experiments.—A measured volume of the hydrazine sulphate solution was placed in a distilling flask of about one liter capacity. Through a separatory funnel was introduced a measured volume of the ammonium metavanadate solution. A slow current of air was drawn through the flask in order to carry the hydronitric acid through the condenser into the absorption apparatus. This absorption apparatus consisted essentially of an Erlenmeyer flask (150 cc.) and a Muencke gas wash bottle. The Erlenmeyer flask was provided with a two-hole stopper through which passed the end of an adapter (connected with the condenser) dipping beneath the surface of the absorbing solution. After passing through the flask the gas was led through a second quantity of the same solution in the Muencke gas wash bottle.

The absorbing solution was prepared by adding 2 cc. of sodium acetate solution (10 g. in 100 cc.) and 5 cc. of silver nitrate solution (10 g. in 100 cc.) to 35 cc. of water. Any hydronitric acid evolved from the reacting mixture was precipitated in the form of silver trinitride. The presence of sodium acetate decreases the solubility of the silver trinitride[1]. In every experiment complete absorption of the acid was effected in the Erlenmeyer flask. The yield of hydronitric acid was determined by the method of Dennis and Isham.[2]

Results Obtained in the Experiments.—Four series of experiments were performed in order to ascertain the effect upon the yield of hydronitric acid of varying (1) the temperature at which the reaction is permitted to take place, (2) the amount of metavanadate solution used, (3) the method of introducing the metavanadate solution and (4) the amount of sulphuric acid present. The results of the different series of experiments are given respectively in Tables I to IV.

[1] Dennis and Isham, This Journal 29, 18 (1907).

[2] loc. cit.

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TABLE I.

Number of Experiment	$N_2H_4H_2SO_4$ (100 gr. per L.) cc.	NH_4VO_3 Solution cc.	NH_4VO_3 per 100 cc. gr.	Conc. H_2SO_4 per 100 cc.	Temperature	Ag Cl obtained gr.	Yield HN_3 per cent.
1	30	100	1.2709	12.8 cc.	20°	0.00345	2.09
2	30	100	1.2709	12.8	60°	0.0049	2.97
3	20[1]	100	1.2709	12.8	60°	0.00485	2.94
4	30	100	1.2709	12.8	100°	0.0126	7.62
5	30	100	1.2709	12.8	100°	0.01215	7.35

In the sixth column is given for each experiment the highest temperature to which the reacting mixture was heated. As this temperature was raised larger yields of hydronitric acid were obtained. This is at least partially attributable to the fact that the acid formed by the reaction is not completely distilled over into the absorption apparatus unless the temperature is raised to 100°. In these experiments the metavanadate was added at once, with the result that the yield of acid even at 100° was not so high as when the solution was added drop by drop under similar conditions (see experiment 6).

The most satisfactory procedure was found to be as follows. The reacting mixture was maintained at a temperature of 80° during the addition of the metavanadate solution. The solution was then brought to the boiling point and was held at that temperature for a few minutes in order to effect the complete removal of the hydronitric acid from the mixture. This procedure was followed in all the experiments recorded in tables II, III and IV.

TABLE II.

Number of Experiment	$N_2H_4H_2SO_4$ (10 gr. per L.) cc.	NH_4VO_3 Solution cc.	NH_4VO_3 per 100 cc. gr.	Conc. H_2SO_4 per 100 cc.	AgCl obtained gr.	Yield HN_3 per cent.
6	20[1]	100	1.2709	12.8 cc.	0.0207	12.52
7	30	100	1.0811	12.8	0.01735	10.50
8	30	100	0.9009	12.8	0.01845	11.16
9	30	100	0.7205	12.8	0.0166	10.04
10	30	100	0.5405	12.8	0.0135	8.17

In experiments, 7, 8, 9 and 10 the amounts of ammonium metavanadate solution employed correspond to 12, 10, 8 and 6 molecules, respectively of the salt for every 3 molecules of hydrazine sulphate. In all of these experiments the metavanadate solution was added drop by drop after the hydrazine sulphate solution had been heated to 80°. From these experiments it is apparent that as a general rule the formation of hydronitric acid is facilitated, within certain limits, by increasing the amount of ammonium metavanadate.

TABLE III.

Number of Experiment	$N_2H_4H_2SO_4$ (10 gr. per L.) cc.	NH_4VO_3 Solution cc.	NH_4VO_3 per 100 cc. gr.	Conc. H_2SO_4 per 100 cc.	Method of adding	AgCl obtained gr.	Yield HN_3 per cent.
11	30	100	1.0811	12.8	At once	0.0135	8.17
7	30	100	1.0811	12.8	Drop by drop	0.01735	10.50
12	30	100	0.9009	12.8	At once	0.01055	6.38
8	30	100	0.9009	12.8	Drop by drop	0.01845	11.16
13	30	100	0.7207	12.8	At once	0.0135	8.17
9	30	100	0.7207	12.8	Drop by drop	0.0166	10.04

[1] 15 gr. $N_2H_4.H_2SO_4$ per liter.

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In experiments 11, 12 and 13 the entire quantity of ammonium metavanadate solution was added at the outset. It is obvious that when the solution is added drop by drop the yield of hydronitric acid is materially increased.

Table IV.

Number of Experiment	$N_2H_4H_2SO_4$ (10 gr. per L.) cc.	NH_4VO_3 Solution cc.	NH_4VO_3 per 100 cc. gr.	Conc. H_2SO_4 per 100 cc.	AgCl obtained gr.	Yield HN_3 per cent.
14	30	100	0.9009	6.4	0.0181	10.95
8	30	100	0.9009	12.8	0.01845	11.16
15	30	100	0.9009	19.2	0.0224	13.55
16	30	100	0.9009	19.2	0.0169	10.23
17	30	100	0.9009	25.6	0.0200	12.10
18	30	100	0.9009	38.4	0.01285	7.78
19	30	100	0.9009	76.8		

From these experiments it appears that when the concentration of sulphuric acid is chosen as indicated for experiment 15, the maximum yield of hydronitric acid is obtained. In experiment 16 the metavanadate solution was added more rapidly than in the preceding case, with the result that the yield of the acid was considerably reduced. In all other experiments the solution was added slowly drop by drop.

Identification of the Hydronitric Acid Formed.—The properties of the acid and of its silver salt were studied almost exactly in the manner recommended in a previous article.[1] The percentage of silver in the silver salt was determined with the following results: (1) 0.21635 gram of the salt gave 0.20605 gram of silver chloride; (2) 0.21735 gram of the salt gave 0.20680 gram of silver chloride. This corresponds to 71.69 and 71.62 per cent. silver (theory, 71.97 per cent.), or to 3.04 and 3.05 atoms of nitrogen per atom of silver. For all calculations in the present article the atomic weights recommended by the International Committee for 1907 have been employed.

In order to ascertain whether the amount of ammonia present undergoes increase or decrease during the course of the reaction the series of experiments recorded in Table V was performed. In experiments 1, 2, 3 and 4, 50 cc. of ammonium metavanadate solution (containing 12.85 grams of the salt and 128 cc. of pure concentrated sulphuric acid per liter) were added slowly to 10 cc. of hydrazine sulphate solution (containing 15 grams per liter) at a temperature of about 80°. The solution was then made alkaline by the addition of a certain excess of sodium hydroxide solution, and the ammonia was distilled, with the usual precautions, into a measured excess of fifth normal hydrochloric acid. The amount of ammonia was determined by titrating back with fifth normal sodium hydroxide solution. In the two blank experiments 5 and 6, 50 cc. of ammonium metavanadate solution were employed, but no hydrazine sulphate solution.

[1] Browne, This Journal 27, 551-555 (1905).

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TABLE V.

Number of Experiment	Total wt. NH_3 gr.	NH_3 formed during reaction gr.	Per cent. NH_3 formed
1	0.09353	0.00174	17.7
2	0.09327	0.00148	15.1
3	0.09370	0.00191	19.5
4	0.09388	0.00209	21.3
5	0.09179		
6	0.09179		

The amount of ammonia formed in the course of the first four experiments was ascertained in each case by subtracting the total weight of ammonia obtained in experiment 5 (or 6) from the total weight of ammonia obtained in each of the first four experiments. The percentages of ammonia formed were calculated on the basis of the equation suggested in a subsequent paragraph, and used by the authors in calculating the percentage yields of hydronitric acid.

On the Use of Ammonium Metavanadate in the Determination of Hydrazine.--Hofmann and Küspert[1] have recommended the use of ammonium meta vanadate in the determination of hydrazine. The procedure followed by these investigators consisted in the slow addition of an excess of ammonium metavanadate solution strongly acidified with sulphuric acid to the hydrazine sulphate solution. When the evolution of nitrogen (which lasts for about 20 minutes) had ceased, the solution was warmed for several minutes to about 60°. The amount of metavanadate that had been reduced was then determined by titration with permanganate solution. In addition to this volumetric method Hofmann and Küspert also suggested the simultaneous measurement of the nitrogen evolved from the mixture. In effecting this operation the reaction was conducted in a current of carbon dioxide by means of which the evolved nitrogen was carried into the measuring apparatus.

In 1899 Rimini[2] after reviewing several different methods for the determination of hydrazine made the statement that the above method was undoubtedly the best of those considered.

The reaction was considered by Hofmann and Küspert to proceed in accordance with the following equation :—

$$N_2H_4.H_2SO_4 + 2O = N_2 + 2H_2O + H_2SO_4.$$

In experiments 1 to 6 (Tables I and II) the authors of the present article have used hydrazine sulphate, ammonium metavanadate and sulphuric acid in the proportions employed in the experiments of Hofmann and Küspert. In each case appreciable amounts of hydronitric acid were obtained. In experiment 3 the conditions recommended by Hofmann and Küspert have been exactly duplicated ; the reacting mixture was allowed to stand at room temperature until the effervescence had ceased,

[1] Ber. 31, 64-67 (1897).
[2] Gazz. chim. ital. 29, (1) 265-69 (1899).

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when it was heated to 60° for a few minutes. Even under these conditions, unfavorable as they were to the quantitative removal and absorption of the hydronitric acid formed, a yield of nearly three per cent. was obtained. In experiment 2 the conditions were the same as in experiment 3 except that the hydrazine sulphate solution was more dilute. No very appreciable variation in the yield of acid, however, was observed. In experiments 4 and 5 the yields of hydronitric acid were considerably higher. In experiment 6 the method of adding the metavanadate solution was modified and the most favorable temperature conditions were chosen. In this case 12.52 per cent. of hydronitric acid were produced.

For the sake of simplicity the percentage yields of hydronitric acid and ammonia have both been calculated on the basis of the equation

$$2N_2H_4 + 2O = HN_3 + NH_3 + 2H_2O.$$

From the fact, however, that the yields of ammonia under the most favorable conditions were found to be higher than the yields of hydronitric acid, it is apparent that the secondary reaction does not proceed quantitatively in accordance with this equation.

The magnitude of the error introduced as a result of the secondary reaction indicated by the above equation obviously depends upon the character of the analytical method chosen. If the oxidimetric method is employed, the percentage error will be numerically smaller than the percentage yield of hydronitric acid, while if the gasometric method is employed the percentage loss of nitrogen due to the formation of hydronitric acid should be numerically equal to the percentage yield of the acid.

In the four experiments performed by Hofmann and Küspert it was found that one molecule of hydrazine sulphate required 1.996, 1.964, 1.959 and 1.939 atoms of oxygen (theory, 2 atoms). The mean deficit in consumed oxygen (0.0355 atom oxygen per molecule of hydrazine sulphate or 1.78 per cent. deficit in oxygen), corresponds to a yield of 3.55 per cent. of hydronitric acid, provided that the absence of possible errors arising from other sources be assumed.

In order to ascertain experimentally the ratio existing between the errors to which the two methods are respectively subject, a series of determinations has been made of the volume of nitrogen liberated and of the amount of oxygen consumed by the oxidation of a measured amount of hydrazine sulphate. In these experiments a Lunge nitrometer was employed, but the ordinary gas evolution bottle was replaced by a 125 cc. Erlenmeyer flask provided with a small test tube placed in a slanting position. This flask was immersed in a beaker filled with water for the purpose of avoiding errors due to changes in temperature. The hydrazine sulphate and ammonium metavanadate solutions were identical in composition with those employed by Hofmann and Küspert, and the

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amount of each solution used was also the same as that employed by these investigators (i.e., 10 cc. of hydrazine sulphate solution containing 15 gr. per liter, and 50 cc. of ammonium metavanadate solution containing 12.85 gr. of the salt and 128 cc. of concentrated sulphuric acid per liter were used). After the flask had been brought to room temperature by immersing it in the beaker of water for some time, the two solutions were mixed in the flask, and with frequent shaking were allowed to remain at room temperature until the greater part of the gas had been evolved. The temperature was then raised to 60° for a few minutes, in order to effect the complete evolution of the gas. After the apparatus had been again brought to room temperature, the volume of gas was carefully measured. Since water was used as the confining liquid, corrections for the tension of aqueous vapor were introduced. The amount of oxygen consumed was in each case determined by titration of the residual solution (after diluting to 250 cc.) with a solution of potassium permanganate containing 7.0274 gr. of the salt per liter. Owing to the difficulty in observing the exact end-point of the reaction a slight excess of permanganate was in each case unavoidably introduced, for which no correction could be satisfactorily made. For this reason the error inherent in the oxidimetric method is to some extent reduced by the compensating error due to the presence of a slight excess of permanganate. The results obtained are appended in Table VI.

Table VI.

Number of Experiment	Nitrogen evolved (0°, 760 mm.) cc.	Deficit in Nitrogen per cent.	Permanganate Solution cc.	Oxygen Consumed gram.	Atoms of Oxygen per molecule hydrazine	Deficit in Oxygen per cent.
1	24.65	4.57	20.4	0.03626	1.966	1.70
2	24.17	6.43	20.45	0.03635	1.971	1.45
3	24.61	4.72	20.5	0.03644	1.976	1.20
4	24.86	3.76	20.7	0.03679	1.995	0.25
5	24.78	4.07	20.6	0.03661	1.985	0.75
6	25.02	3.14	20.65	0.03670	1.990	0.50
Average		4.45				0.975

From the above experiments it is apparent that when the reaction between hydrazine sulphate and ammonium metavanadate in sulphuric acid solution takes place in a Lunge nitrometer the error due to the formation of hydronitric acid averages about 4.5 per cent. in case the gasometric method is employed, or about one per cent. when the oxidimetric method is used.

Summary.—When hydrazine sulphate and ammonium metavanadate are brought together under favorable conditions in the presence of sulphuric acid a secondary reaction takes place (to an extent depending on the conditions chosen) which results in the formation of hydronitric acid and ammonia. Under the most favorable conditions studied by the authors the yield of hydronitric acid, as calculated from the equation

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$2N_2H_4 + 2O = HN_3 + NH_3 + 2H_2O$, amounted to 13.55 per cent. of the theory. The highest yield of ammonia amounted to 21.3 per cent. on the basis of the same equation. The use of ammonium metavanadate in the determination of hydrazine, as recommended by Hofmann and Küspert, is theoretically subject to a percentage error numerically equivalent to the percentage yield of hydronitric acid when the nitrometric method is employed, and to a smaller error when the oxidimetric method is chosen. By the use of a Lunge nitrometer the error was found to be about 4.5 per cent. for the nitrometric method and about one per cent. for the oxidimetric method.

CORNELL UNIVERSITY,
June, 1907.

UNIFICATION OF TERMS USED IN REPORTING ANALYTICAL RESULTS.[1]

BY CYRIL G. HOPKINS, Chairman of Committee from the Association of American Agricultural Colleges and Experiment Stations.

Received July 5, 1907.

In 1904 at the St. Louis meeting of the Association of Official Agricultural Chemists, a committee was appointed on unification of terms used in reporting analysis; and at the Des Moines meeting a similar committee was appointed by the Association of American Agricultural Colleges and Experiment Stations.

These two committees have cooperated in the work assigned and at the last annual meetings made substantially the same report to their respective associations.

Final action on the report was postponed for one year by the Association of Official Agricultural Chemists at Washington last November, in part, because at that time no action had been taken by the broader association of Agricultural Colleges and Experiment Stations, whose annual convention was held a week later at Baton Rouge, at which meeting, however, the report which follows was adopted with the conditions stated:

Report of Committee on Unification of Terms Used in Chemical Analysis.

"Your committee has been working in cooperation with a similar committee from the Association of Official Agricultural Chemists, and the following report is in harmony with a report already made to that association by its own committee, on which action was postponed for one year.

The subject-matter referred to your committee naturally divides itself into two classes, one of which includes soils, fertilizers, ash and other materials whose analysis may be expressed in terms of chemical elements or in simple compounds; while the other class includes foodstuffs, condiments, and other materials whose analysis may best be expressed in terms

[1] Read at the Toronto Meeting of the American Chemical Society, June 28th, 1907.

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of more complex compounds, or groups of compounds, which actually compose or are contained in the material.

Soils, Fertilizers, Etc.

Special efforts have been made during the past two years to secure a full consideration, especially by directors of experiment stations, chemists, and agronomists, of the question whether it is better to continue to report analysis of soils and fertilizers on the basis of oxides (excepting nitrogen, which is already most commonly reported as the element), or to report such analysis on the uniform basis of the elements.

Several circular letters have been sent out, and in answer to this question 85 replies have been received. Of these there were 21 making comments, but expressing no definite or final opinion on the question; there were 16, including 12 chemists who favor retaining the present system; while there were 17 chemists, 16 agronomists, and 15 directors and other officers, or 48 in all, who expressed definite opinions in favor of adopting the uniform system of elements.

In view of these facts, and providing concurrent action is taken by the Association of Official Agricultural Chemists and the American Chemical Society, your committee favors the adoption of the element system for reporting analytical results in the analysis of soils, ashes, and fertilizers as rapidly as possible, and recommends that the association urge those responsible for fertilizer legislation to have the laws changed if necessary, and as soon as practicable to meet with these recommendations, if concurred in.

This would necessitate the adoption of the dual system of expressing results temporarily in some States, but it is hoped that when fertilizer laws are adopted to meet these requirements some definite time will be set, at the expiration of which only the element system will appear on the bags or tags. It is therefore suggested that no other terms than those of the element system be allowed after the year 1916.

Your committee also recommends, provided the foregoing is adopted, that this association adopt some definite form for stating the composition of fertilizers and fertilizer materials. The following form is suggested.

Elements Guaranteed.	Per Cent.
Available nitrogen	
Inert nitrogen	
Available phosphorus	
Inert phosphorus	
Available potassium	
Inert potassium	

We recommend that the terms "available" and "inert" shall be used in harmony with the construction placed upon them by the Association of Official Agricultural Chemists.

The committee also recommends that in case of the adoption of the

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foregoing there be required to be printed on the bag or on the tag to be attached to the bag or to accompany fertilizers sold in bulk an explanatory statement naming the materials in which the plant food is carried, as, for example:

The plant food guaranteed in this fertilizer is carried in cotton-seed meal, potassium chloride, and acid phosphate.

Foodstuffs, Condiments, Etc.

In the case of foodstuffs, condiments, etc., your committee recommends in the statement of analytical results the use of names of compounds (or groups of compounds) actually present as such in the material, this being in accordance with the present practice.

Your committee asks for further time in which to consider the more complete unification of systems for reporting results of analysis of some miscellaneous materials, as insecticides, baking powders, etc.

It is further recommended that this association appoint a committee to aid (preferably in cooperation with a similar committee from the Association of Official Agricultural Chemists) in trying to bring about both national and international uniformity in the reporting of analytical results."

This report with the conditions stated as presented by the committee was adopted by the Association of American Argicultural Colleges and Experiment Stations, and on behalf of that association I now present this report to the American Chemical Society and ask for its endorsement.

UNIVERSITY OF ILLINOIS,
Urbana, Ill.

CONTRIBUTION TO THE DETERMINATION OF PHOSPHORIC ACID VOLUMETRICALLY.

BY. W. D. RICHARDSON.
Received July 11th, 1907.

It is a fact fairly well known among agricultural chemists that when phosphoric acid is determined in acid phosphate by the Pemberton volumetric method or its usual modifications results are obtained which do not agree with those obtained by the gravimetric method of the A. O. A. C. and the error frequently amounts to + 1 per cent. P_2O_5. Inasmuch as the volumetric method in general agrees well with the gravimetric and as it is a desirable method to use, a search was made in this laboratory for the substance which caused the discrepancy.

A check sample of an ordinary run of acid phosphate was sent out to a number of chemists and the results were in accord with previous experience, that is differences amounting in the extreme case to 1.2 per cent. P_2O_5 were recorded. Following this, mixtures of microcosmic salt and the impurities usually present in acid phosphate, namely lead salts, fluorides, arsenic compounds and silicic acid were made and the P_2O_5 in them

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determined by the modified Pemberton method of the A. O. A. C. In no case could any serious discrepancy be observed. About this time, Mr. J. F. Wilkinson, suggested that sulphuric acid was the disturbing substance and that if it were previously removed by means of barium chloride the volumetric method could be applied as usual and accurate results obtained. This proved to be the case. Experiments were conducted with solutions of phosphate rock in hydrochloric acid to which were added respectively sulphuric acid, sodium sulphate and calcium sulphate, in which the P_2O_5 was determined by the volumetric method. The results did not agree with those obtained by the A. O. A. C. gravimetric method when working on the same solutions and varied from 0.2 to 1.00 per cent. P_2O_5 above the gravimetric method. In other words the sulphate ion invariably caused greater or smaller discrepancies. The work shows the necessity of excluding sulphuric acid from the reagents used to dissolve phosphate containing fertilizers for analysis.

The following working method was adopted for fertilizers, particularly acid phosphate, containing sulphates. A long and thorough trial has demonstrated its accuracy and value.

Weigh two grams into a 250 cc. flask, digest by boiling with 30 cc. concentrated nitric acid and 5 cc. concentrated hydrochloric acid, then add 10 cc. water and boil for five minutes. Add 25-30 cc. of 10 per cent. barium chloride solution, cool and make up to volume. Filter through a dry filter, rejecting the first portion of the filtrate and take 25 cc. for the determination. From this point on follow the A. O. A. C. modification of the Pemberton method.

In the presence of sulphates, sulphuric acid or a sulphate was always found by analysis in the yellow precipitate of ammonium phospho-molybdate and it is altogether probable that a complex ammonium sulpho-molybdate is formed under the conditions of phosphoric acid precipitation by ammonium molybdate which has the acid nature of ammonium phospho-molybdate and therefore reacts with alkali and phenolphthalein similarly to the latter.

The analytical work mentioned was carried out in large part by Mr. John Jepsen of this laboratory.

LABORATOY OF SWIFT & CO.,
Chicago.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

A GASOMETRIC METHOD FOR THE DETERMINATION OF HYDROGEN PEROXIDE.

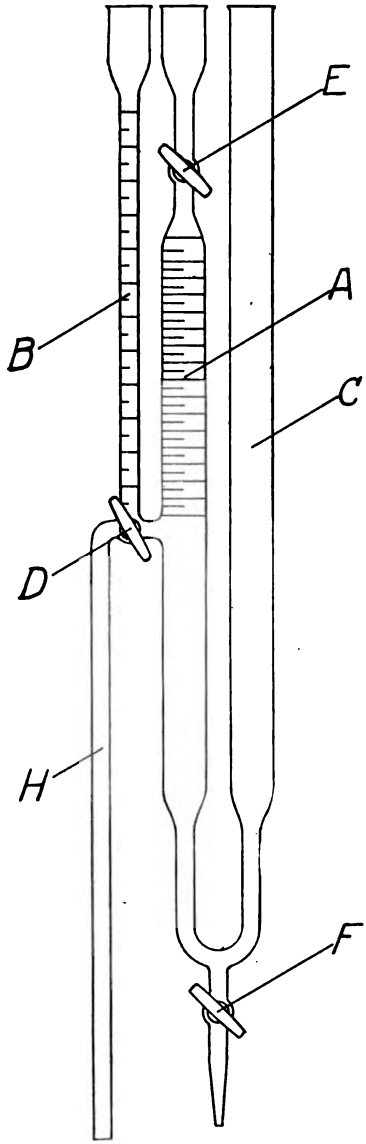
BY WILLIAM M. DEHN.

Received June 18, 1907.

The apparatus depicted in the figure was designed as an ureometer; its construction and the application to this purpose are described in another

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contribution[1]. It has been found that this instrument can be used also



for rapid and accurate determination of hydrogen peroxide. The reaction involved—

$H_2O_2 + NaBrO = NaBr + H_2O + O_2$ is immediate[2] and, as shown below, is sharply quantitative.

Method.—The stopcock E is opened and the stopcocks D and F are

[1] Z. anal. Chem. **45**, 604.

[2] Lunge, Ber. **19**, 1886; Tanatar, Ber. **32**, 1013; Forester, J. pr. Chem. **63**, 141.

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closed, then the solution of sodium hypobromite[1] is poured in at the top of C until it fills the tubes A and C to some point above the stopcock E. The stopcock E is then closed and the stopcock F is opened so that the hypobromite in C may run down to the constricted portion—the hypobromite in A is then sustained by atmospheric pressure. The stopcock D[2] is turned from the position shown in the figure and is so controlled that B may first be washed with a little of the hydrogen peroxide and then be filled with the same to a readable height on the scale. Upon turning D so as to admit a regulated volume of the hydrogen peroxide solution, an immediate evolution of oxygen results. After admitting most of the hypobromite held above E, and letting stand for a minute or two so as to drain properly, the columns of hypobromite in A and C are brought to the same level, the volume of oxygen is read, and its weight and that of the corresponding hydrogen peroxide are calculated by the usual formulas.

A sample of hydrogen peroxide, whose specific gravity at 19° was 1.0133, gave by decomposition with a sodium hypobromite solution the following data:

Experiment	Vol. H_2O_2	Vol. O_2	Temperature	Atmospheric Pressure	Vapor Pressure NaBrO	Weight O_2	Per Cent. H_2O_2
1	5 cc.	11.40	26.8	742.2	19.75	0.01411	2.621
2	"	11.43	"	"	"	0.01414	2.628
3	"	11.37	"	"	"	0.01408	2.614
Average	"	11.40	"	"	"	0.01411	2.621
The same sample by the iodide titration method =							2.625
" " " " permanganate " =							2.641

Other samples of hydrogen peroxide gave by this gasometric method results that coincided with the most careful analysis by the iodine titration method.

For most accurate analysis the vapor-pressures of the hypobromite solution used must be taken into account. The usual solution of hypobromite (sp. gr. 1.25) was found to exert the following vapor-pressures:

Temperature	Vapor-Pressure. NaBrO	H_2O	Difference
4	1.1 mm.	6.1 mm.	5.0 mm.
8	1.8	8.0	6.2
12	3.3	10.5	7.2
16	5.3	13.6	8.3
20	8.6	17.4	8.8
24	12.8	22.2	9.4
28	18.0	28.1	10.1
32	24.0	35.4	11.4
36	29.5	44.2	14.7
40	36.0	55.0	19.0

[1] The usual method of preparation of this solution is as follows: dissolve 100 g. of caustic soda in 250 cc. of water and to each 100 cc. of this solution add 10 cc. of bromine and finally to the resulting solution add an equal volume of water. The specific gravity of the solution is 1.25. It need not be freshly prepared, nor is its efficiency rapidly impaired by repeated use. However it must be remembered that on diluting its vapor-pressure is increased and, by neglect of the same, errors approaching 1 per cent. may be introduced.

[2] This stopcock is ground or plugged so as to deliver only in the two directions of a right angle triangle.

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Weight in milligrams of H_2O_2 corresponding to one cubic centimeter of moist oxygen.

t/mm.	728	732	736	740	744	748	752	756	760	764	768
4°	1.2664	1.2734	1.2802	1.2872	1.2942	1.3011	1.3081	1.3151	1.3222	1.3290	1.3359
8	1.2463	1.2531	1.2600	1.2669	1.2736	1.2805	1.2876	1.2944	1.3014	1.3081	1.3150
12	1.2251	1.2317	1.2387	1.2454	1.2522	1.2589	1.2657	1.2726	1.2823	1.2860	1.2928
16	1.2044	1.2111	1.2178	1.2245	1.2311	1.2378	1.2444	1.2512	1.2578	1.2946	1.2713
20	1.1817	1.1884	1.1948	1.2015	1.2080	1.2145	1.2213	1.2279	1.2345	1.2410	1.2475
24	1.1583	1.1649	1.1719	1.1777	1.1843	1.1907	1.1972	1.2036	1.2100	1.2169	1.2230
28	1.1345	1.1411	1.1476	1.1538	1.1603	1.1665	1.1731	1.1796	1.1857	1.1922	1.1986
32	1.1085	1.1149	1.1213	1.1275	1.1338	1.1401	1.1465	1.1528	1.1589	1.1562	1.1715
36	1.0843	1.0905	1.0967	1.1030	1.1093	1.1155	1.1214	1.1279	1.1341	1.1402	1.1465
40	1.0605	1.0666	1.0725	1.0786	1.0849	1.0909	1.0971.	1.1033	1.1094	1.1155	1.1216

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Here the vapor-pressures of the hypobromite solution are seen to be considerably less than the pressures of pure water. The effect of *different concentrations* of hypobromite may be seen in the following table:

NaBr Solution	H_2O added	Specific Gravity	Vapor Pressure	Difference H_2O
I	0	1.253	10.70	9.56
I	1	1.131	12.77	7.49
I	3	1.062	15.73	4.53
I	7	1.033	17.50	2.76
I	∞	1.000	20.26	0.00

In the preceding table, (p. 1318) cubic centimeters of oxygen under various conditions of temperature and pressure are calculated to milligrams of hydrogen peroxide, corrections for the aqueous pressure of the hypobromite (sp. gr. 1.25) and the effect of temperature on the barometric column are included.

By the use of this new gasometer, this hypobromite method and the table for calculating, the determination of hydrogen peroxide is made not only rapid and accurate but the necessity of preparing and correcting standard solutions is avoided and the presence of the usual preservatives in the peroxide solution can be neglected.

URBANA, ILL.
June 14th, 1907.

THE ACTION OF PHOSPHORUS OXYCHLORIDE ON 1,8-NAPHTHYLAMINE SULPHONIC ACID.

BY FREDERIC DANNERTH.
Received July 2, 1907.

As early as the year 1887 Schultz made short mention of an inner-anhydrid of 1,8-naphthol-sulphonic acid which he had prepared for the first time by heating this latter compound with concentrated sulphuric acid. The pure product appears as colorless difficultly soluble prisms having a melting point of 154°. Because of its similarity to the lactones he named the new substance Naphtsultone. Our knowledge of the lactone of hydroxy-benzoic acid and the lactam of amino-benzoic acid suggests at once the possibility of an amino derivative similar to this naphtsultone. Dressel and Kothe in their researches on the sulphonation of naphthalene derivatives succeeded in preparing compounds of this type.

On treating 1,8-naphthylaminesulphonic acid with concentrated sulphuric acid and heating, they obtained a body which according to the analysis and its chemical behavior seemed to be a sulphonic acid of an inner-anhydrid, which they then called naphtsultam. Unfortunately this anhydrid formation was always accompanied by sulphonation in the nucleus so that it at that time appeared impossible to obtain the pure mother-substance. Bearing this in mind an attempt was made to remove the molecule of water with a reagent which would leave the nucleus in-

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tact. For this purpose phosphorus oxychloride proved to be admirably adapted.

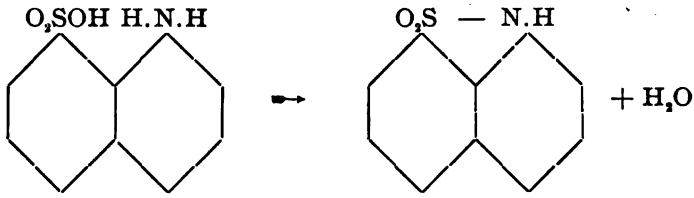
1-8-Naphtsultam. 261 grams of the potassium salt of 1-8-naphthylamine sulphonic acid were pulverized and placed in a flask containing three times that weight of phosphorus oxychloride. After attaching a reflux condenser the whole was heated in an oil bath to 130°. At 100° the offensive vapors of hydrochloric acid are given off and must be led into a flue. To hasten the reaction the flask is shaken repeatedly. After the irritating vapors have ceased to be given off the heating is continued until the contents of the flask ceases to form a dyestuff when diazotized and developed. As a rule the reaction is complete after three hours. The removal of the excess of phosphorus oxychloride requires some care because of the mud like consistency of the contents of the flask. This last operation is not necessary but preferable. Finally the contents of the flask are poured on chipped ice or better still the chips of ice are introduced into the previously cooled flask. The gray product is filtered off by means of a suction pump and the greater part of the phosphoric acid removed by repeated washing. The crude naphtsultam may be recrystallized from benzene after thoroughly drying or from water without previous drying. In both cases a small quantity of charcoal is added to decolorize and remove the side products. On recrystallizing from hot water, needles 2–3 centimeters in length are obtained. Melting point: 177°–178°. Analysis:

$C_{10}H_7O_2NS$ (205.15)

Calculated: C = 58.44 H = 3.43 N = 6.84 S = 15.62

Found : 58.43 3.4 6.83 15.70

Instead of the theoretical yield of 205 grams only 119 grams or 60 per cent. of this is obtained. The reaction may be formulated as follows:



The analysis of the compound and its behavior toward nitrous acid and toward fused caustic potash, seemed to support this view. In the same manner as the closing of the ring could be effected only by very strong reagents the breaking of the ring can only be done by such methods as the potash fusion. At low temperatures this yields 1-8-amino-naphthol (M.P. 96°), at high temperatures it yields 1-8-dihydroxy-naphthaline. (M.P. 140°). Naphtsultam is soluble in hot water, ether, warm benzene, chloroform, glacial acetic acid, and alcohol. Many of these solutions possess an applegreen fluorescence. The solubility in alkaline hy-

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droxides is due to the formation of metallic salts. The "imino" group has assumed an acid nature due to the influence of the negative SO_2 group. The sodium salt was prepared by treating the alcoholic solution of the naphtsultam with dilute sodium hydroxide. Beautiful yellow crystals separate and may be recrystallized from dilute alcohol. The salt was dried at 150° and analyzed.

Analysis:

$C_{10}H_6O_2NSNa$ (227.19)
Calculated : 10.15 per cent. Na
Found : 10.28

Naphtsultam forms with the alkaline earths difficultly soluble yellow compounds. From all these salts the naphtsultam may be recovered by acidifying with dilute hydrochloric acid. Below are given some of the reactions of the new body:

$K_2Cr_2O_7$: gives a dark blue flocculent precipitate with the sultam in acetic acid solution.

$FeCl_3$: gives with alcoholic solution of the sultam a dark blue precipitate.

Amyl nitrite : 4.1 grams of naphtsultam were dissolved in alcohol acidified with hydrochloric acid and then treated with 2.35 grams of amyl nitrite. After warming a few minutes and then cooling a red crystalline body separates.

The sodium salt of naphtsultam yields dyes when coupled with diazo-bodies.

O-diamino-toluene gives a violet dye.

β-naphthylamine gives a blue dye.

ω-Methyl Naphtsultam. 2 grams of naphtsultam were heated to 100° in a Carius tube for four hours with four grams of methyl iodide and 0.4 grams of sodium. On removing the tube the new compound could be seen in the form of laminated crystals. After recrystallization from methyl alcohol it showed a melting point of 125°. The compound is easily soluble in alcohol with green fluorescence.

Analysis:

$C_{11}H_9O_2NS$ (219.16)

Calculated	C = 60.23	H = 4.13	N = 6.40
Found	60.07	4.19	6.41

Ethyl Naphtsultam. This compound was prepared in a manner analogous to the methyl derivative. The contents of the Carius tube were poured into cold water, and the precipitated ethyl derivative recrystallized from ethyl alcohol. The alcoholic solution exhibits an emerald green fluorescence. (M.P. 85°).

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Analysis :

$C_{12}H_{11}O_2NS$ (233.18)

Calculated : 6.02 per cent. N

Found : 6.12

1-Methyl-Naphthylamine-8-Sulphonic Acid. As a means of proving the identity of methyl naphtsultam this latter compound was saponified. If the methyl group is linked to the nitrogen atom, the melt should yield the above mentioned sulphonic acid ; if on the other hand the methyl group is linked to an oxygen atom the saponification will yield an amino-sulphonic acid which will be capable of diazotization. The absence of an amino group in the present case was proved by the fact that the compound would absorb no nitrous acid.

Preparation : In a small Erlenmeyer flask two grams of potassium hydroxide were heated with a few drops of water and about one gram of methyl naphtsultam introduced. The substance melts, is saponified and falls to the bottom as an insoluble white mass. The excess of potash solution is poured off and the difficultly soluble potassium salt is boiled with a large amount of water, filtered, acidified with hydrochloric acid and allowed to cool slowly. The gray crystals which separate are filtered off, washed with alcohol and recrystallized from boiling water. They possess no melting point. This compound is especially interesting as Fussgänger in his attempts at preparing it by direct methods always obtained the dimethyl derivative.

Analysis :

Found : C = 55.28 H = 5.03 N = 6.02 S = 13.15 per cent.

Calculated for methyl naphthylamine sulphonic acid ($C_{11}H_{11}O_3NS$) 237.18

C = 55.65 H = 4.67 N = 5.92 S = 13.52 per cent.

Calculated for naphthylamine sulphonic acid ($C_{10}H_9O_3NS$) 223.17

C = 53.76 H = 4.06 N = 6.29 S = 14.36 per cent.

Di-Brom-Naphtsultam. The action of bromine on naphtsultam seems to vary with the form in which this substance is allowed to act. Bromine water brominates first and then exercises an oxidizing action. The addition of the first few drops causes the precipitation of a white granular body which soon changes color passing from pale green to dark blue. Pure bromine on being added drop by drop to the acetic acid solution of naphtsultam causes the precipitation of the white dibromide, which after recrystallization from chloroform had a melting point of 239°. The raw product turns a dark blue on boiling with alcohol.

Analysis :

$C_{10}H_5O_3NS$ (363.0)

Calculated : 44.05 per cent. Br

Found : 43.82

Mono-Nitro-Naphtsultam. In order to obtain this body it was neces-

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sary to prevent the formation of higher nitro bodies by using dilute nitric acid. One gram of naphtsultam was treated with a mixture of 5 cc. nitric acid, (sp. gr. 1.4) and 5 cc. of water. The white sultam gradually assumes a yellow color. After completion of the reaction it is filtered off and recrystallized from glacial acetic acid plus acetone. Melting point of the crystals 253°.

Analysis:

$C_{10}H_6O_4N_2S$ (250.18)

Calculated: 11.2 per cent. N

Found : 11.31

2,4-Dinitro-Naphtsultam. By the action of concentrated nitric acid (sp. gr. 1.45) two nitro groups can be introduced into the nucleus of the sultam. Two grams of dry naphtsultam were treated in a small Erlenmeyer flask with excess of nitric acid. The evolution of nitrogen oxides takes place immediately. After a few minutes a few small particles of ice are placed in the flask, whereby the nitro body separates out. On recrystallization from alcohol beautiful six-sided prisms containing acetone of crystallization are obtained. The crystals melt at 259° and then decompose. In order to determine the position of the nitro groups the 2,4-disulphonic acid of the sultam was made use of. The sulphonic groups were replaced by nitro groups according to the method of Dressel and Kothe.

40 grams of the sodium salt of naphtsultam 2,4-disulphonic acid were mixed in the cold with 200 grams of concentrated sulphuric acid. The mixture was cooled and then 40 grams concentrated sulphuric acid plus 22 grams of nitric acid (1.4) were added. The temperature should not rise above 20°. After all the acid has been added the mixture is heated to about 35° in order to complete the reaction. It is now poured on chipped ice and the body which separates is recrystallized from acetone. The melting point, reactions and analysis showed that this compound was identical with the original.

Analysis:

$C_{10}H_5O_6N_3S$ (295.21)

Calculated: 14.27 per cent. N

Found : 14.17

2,4-Diamino-Naphtsultam. Although it was impossible to prepare this compound, owing to its rapid oxidation and ready solubility, the hydrochloride was obtained with comparative ease.

In a small Erlenmeyer flask five grams of stannous chloride and 10 cc. of concentrated hydrochloric acid were heated and one gram of dinitro naphtsultam was introduced. After heating slightly the reaction sets in and soon all goes into solution; on cooling, the dihydrochloride is obtained in the form of fine needles. The pale yellow crystals obtained on re-

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crystallizing from hot dilute alcohol quickly undergo oxidation when moist, thereby assuming a red color. The salt was dried in a vacuum dessicator over caustic potash.

Analysis:

2 HCl. $C_{10}H_{11}O_2N_3S$ (308.15)

Calculated : 23.04 per cent. Cl

Found : 22.9

The pure diamine is readily decomposed. The salts crystallize well, are soluble in water, difficultly soluble in dilute hydrochloric acid. Ferric chloride colors the aqueous solution a deep wine red. Although this is a diamine the characteristic "Bismarck brown" coloration is not obtained with nitrous acid owing to the fact that both the ortho and para positions to the amino group are occupied. On coupling the diazo compound with a naphtol a red-brown dye is obtained. On boiling the aqueous solution of the diamine hydrochloride the liquid becomes turbid but on cooling, beautiful black crystals insoluble in water are deposited.

On mixing the diamine hydrochloride with a small quantity of water it at first dissolves but is soon precipitated in the form of deep-yellow crystals. On recrystallizing from boiling water they were obtained pure and proved to be the mono-hydrochloride.

Analysis:

$C_{10}H_9O_2N_3S$. HCl

Calculated : 13.06 per cent. Cl

Found : 13.28

2,4-Di-Acetyl-Diamino-Naphtsultam. In order to better characterize the diamine just obtained, its acetyl derivative was prepared. Anhydrous sodium acetate was heated with freshly distilled acetic anhydride and the diamine added. The acetyl derivative soon separates as a greenish-yellow body. After washing on the filter plate with water, acetic acid, alcohol and ether it was recrystallized from nitrobenzene. Small needles having a melting point of 290° were obtained.

Iso-Naphtsultam. On attempting to acetylate the naphtsultam a body was obtained which on analysis gave figures corresponding to the normal naphtsultam. The structural formula of this latter compound at once suggested that a rearrangement of the atoms had taken place, which would be a very interesting case of Desmotropism. That this was the case was proven by several reactions.

Preparations of the Iso-Body : 2 grams of naphtsultam were treated with two grams of boiling acetic anhydride for 3/4 of an hour in a small Erlenmeyer flask equipped with a condenser tube. Toward the end of the reaction beautiful rhombic crystals separate whereupon all is poured into a beaker of water in order to remove the excess of acetic anhydride. On recrystallizing from boiling alcohol crystals having a melting point of

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188° are obtained. The crystals are soluble in chloroform, acetic acid and benzene.

Analysis :

$C_{10}H_7O_2NS$ (205.15)

Calculated :	C = 58.49	H = 3.44	N = 6.84
Found :	59.29	3.83	6.96

Although the carbon value is slightly high, the molecular weight determination by the freezing point method gave good results.

Benzene constant = 50.

0.1650 g. dissolved in 15.94 g. benzene. Dep. = 0.255°

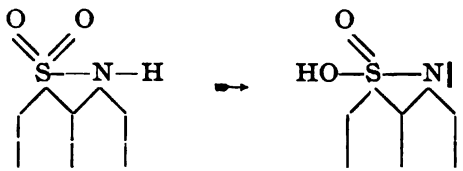
Molecular weight calculated : 205.2

found : 203.0

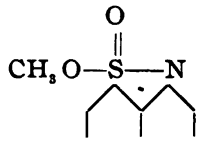
0.1320 g. dissolved in 22.73 g. benzene. Dep. = 0.140°

found : 207.0

These figures indicate sufficiently that a union of two molecules did not take place, but that the atoms had suffered a rearrangement according to he formula :



The iso-naphtsultam is soluble in boiling 50 per cent. sodium hydroxide with the formation of a yellow sodium salt. On acidifying this solution a white precipitate of the normal naphtsultam is obtained. An unsuccessful attempt was made to prepare the silver salt in order to obtain the methoxy derivative :



The usual method of introducing alkyl groups by heating in a Carius tube, as also the method with diethyl sulphate, yielded no results. The main difficulty seems to lie in the instability of the iso-body, in the presence of alkalies. The attempt to prepare the methyl ether by leading hydrochloric acid gas into the mixture of dry methyl alcohol and isonaphtsultam for four hours resulted in the formation of a chlorine derivative, which is soluble in alcohol. The solution was evaporated and the substance recrystallized from dilute alcohol. The crystals have a melting point of 200°–201°.

Analysis :

$C_{10}H_6O_2NSCl$ (239.5)

Calculated : 14.80 per cent.

Found : 14.67

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A chlorine derivative having the identical melting point was obtained by leading chlorine into the ice cold solution of iso-naphtsultam for thirty minutes. The substance left on evaporating the solution was recrystallized from a mixture of alcohol and chloroform. The conditions under which this latter body was obtained indicate that the chlorine had entered the nucleus.

Phosphorus pentachloride reacts with iso-naphtsultam at 188°. The melt is a mixture of oxidized bodies soluble partly in ether, in alcohol and in benzene. The ethereal solution gave a small yield of perfect hexagonal crystals not sufficient for an analysis.

Mono-Brom-Iso-naphtsultam. To the chloroform solution of the iso-naphtsultam bromine was added until the solution assumed a permanent yellow color. The white crystalline body obtained on evaporation when recrystallized from glacial acetic acid had a melting point of 162°. The color of the impure compound is changed to blue on boiling with dilute acetic acid.

Analysis :

$C_{10}H_6O_2NSBr$ (284)

Calculated : 11.2 per cent. N 11.29 per cent. S

Found : 27.98 11.32

Mono-Nitro-Iso-napthsultam. One gram of the iso-naphtsultam was treated with an equal weight of nitric acid (sp. gr. = 1.4) in a flask. At first no action is perceptible. On warming slightly the iso-naphtsultam is dissolved with great evolution of heat and on cooling pale yellow crystals are obtained, which when recrystallized from acetic acid show a melting point of 212°.

Analysis :

$C_{10}H_6O_4N_2S$ (250.18)

Calculated : 11.2 per cent. N

Found : 11.3

The body is soluble in a 10 per cent. solution of sodium hydroxide forming an orange-red salt. On acidifying a yellow precipitate is obtained, which on recrystallizion melts at 252°, indicating a reversion to the normal compound.

2,4-Dinitro-Iso-naphtsultam. Fuming nitric acid reacts violently with the iso-body, the reaction being accompanied with a great evolution of heat. The solution deposits yellow crystals which when purified with acetone melt at 256°. If the reaction is not allowed to proceed far enough, the mono-nitro body is obtained. On the other hand the extended action of the hot acid results in the formation of an infusible body. If too much acid has been used the nitro-body will not precipitate on cooling. In this case it can be salted out by adding a solution of caustic soda, taking care that the solution retains a slight acidity.

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Analysis :

$C_{10}H_5O_6N_3S$ (295.21)

Calculated : 14.27 per cent. N

Found : 14.31

On heating this substance with sodium hydroxide and then acidifying the normal dinitro naphtsultam is obtained.

2,4-Dinitro-Naphthalene-8-Sulphonic Acid. If the iso-naphtsultam is heated with an excess of fuming nitric acid, an almost clear solution is obtained. When cool this is filtered with an asbestos filter. The filtrate is almost neutralized with a concentrated solution of potassium hydroxide avoiding at the same time any great increase in temperature. On cooling, the crystals separate and are recrystallized from boiling water. On heating the substance on a platinum foil it does not melt but explodes at about 300°. The yellow solution in sodium carbonate yields large crystals of the sodium salt.

The same sulphonic acid was prepared from the "normal" naphtsultam as also from the naphtsultam-2,4-disulphonic acid on treating these latter compounds with hot fuming nitric acid. This may be taken as proof of the position of the nitro groups. On recrystallizing from hot water, needles two centimeters in length may be obtained.

Analysis :

$C_{10}H_6O_7N_2S$ (298)

Calculated : C 40.26 per cent. N 9.39 per cent.

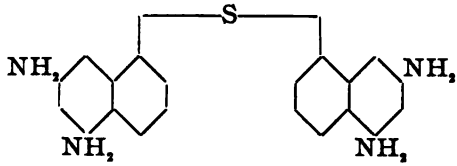
Found : 40.2 9.66

2,4-Diamino-Naphthalene-8-Sulphonic Acid.— One gram of the nitro compound just described was placed in a mixture of 4.5 g. stannous chloride and 15 cc. of concentrated hydrochloride acid. At first a deep red color is produced but on heating all dissolves to a yellow solution. On cooling the flask and contents the hydrochloride separates and may be dried in a desiccator over caustic potash. A further proof of the position of the nitro groups in the preceding compound was the "Bismarck brown" coloration obtained with nitrous acid. Therefore also the position "1" must be unoccupied, otherwise the two molecules could not unite. On moistening the hydrochloride with alcohol or with dilute caustic soda it assumes a blue color. On boiling the aqueous solution and subsequent cooling beautiful black needles are obtained; these possess no melting point.

Oxidation with PbO_2 yields a coloring matter which dyes wool a violet color in acid solution. Vigorous reduction with a boiling mixture of stannous chloride and hydrochloric acid yields a different product. The nitro body is changed in color to a dark brown with evolution of hydrogen sulphide, and the product of the reaction behaves altogether different from the diamine just described. Possibly the sulphonic acid

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group has been reduced to a mercaptan and then with the elimination of hydrogen sulphide the following body was obtained.



In conclusion I wish to thank Professor L. Gattermann for valuable assistance and Professor Carl Duisberg for his kindness in supplying large quantities of raw materials for the experiments.

Germantown, Philadelphia

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS].

AN IMPROVED METHOD FOR THE PREPARATION OF ALKYL CHLORIDES.

WILLIAM M. DEHN AND GRANT T. DAVIS.

Received July 2, 1907.

On account of the variety of reactions into which they enter, the alkyl halides and their preparation are of especial interest and importance. Though quite satisfactory methods for the preparation of the bromides and iodides are in common use, the present methods used for preparing the corresponding chlorides are open to serious objections, principally on account of the smallness of yields. The necessity of preparing considerable quantities of a number of higher alkyl chlorides for another line of research led us to investigate more closely the methods hitherto employed, in order to determine the best conditions and methods for the preparation of these compounds.

The first alkyl chloride was prepared in 1759 by Rouelle, who treated ethyl alcohol with the chlorides of sulphur, antimony, tin, iron, bismuth, and aluminum respectively. In 1801 Basse prepared the same chloride by treating alcohol with gaseous hydrochloric acid and,[1] modified by the addition of zinc chloride[2] in the case of methyl and ethyl alcohols and by heating in sealed tubes the higher alcohols saturated with gaseous hydrochloric acid, this remained the favorite method for many years.

In 1871 Pierre and Puchot,[3] working with propyl and butyl alcohols, discarded the reactions in sealed tubes, in favor of the reaction of phosphorus pentachloride with alcohols[4], and this method of preparation, to-

[1] Balard, Ann. 52, 312; Zincke, Ann. 152, 4; Rossi, Ann. 159, 72; Cross, Ann. 189, 3; Butlerow, Ann. 189, 51; Rohn, Ann. 190, 312; Brocket, Ann. 77 10, 384; Kaschirscky, Russ. Ber. 13, 90.

[2] Groves, Ann. 174, 372. Krüger J. pr., Chem. (2) 14, 195.

[3] Ann. 163, 266.

[4] Cahours, Ann, 37, 164; Borris, Ann. 92, 398; Limpricht, Ann. 103, 81; Butlerow, Ann. 177, 183; Pieverling, Ann. 183, 348; Winogradow, Ann. 191, 131, Wyschnegradsky, Ann. 190, 336; Saytzen, Ann. 179, 321; Butlerow, Bull. soc. chim. 5, 24; LeBel. Bull. soc. chim. 25, 546; Henry, Bull. soc. chim. 41, 363; Mourgues, Ber. 23, 658; Fawosky, Russ. Ber., 19, 425; Grigorowitsch, Pawlow, Russ. Ber. 23, 166.

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gether with its modifications in the use of phosphorus trichloride[1] and phosphorus oxychloride[2], is most commonly recommended in the text books, although Malbot[3] reported "a quantitative yield" of the active amyl chloride when he heated in a sealed tube, alcohol first saturated with gaseous hydrochloric acid and then mixed with one half its volume of fuming aqueous acid. Other methods which have been employed with less success involve the action of chlorine on paraffin hydrocarbons[4] and the action of hydrochloric acid on olefin hydrocarbons.[5]

The general objections to these methods are found to be either the smallness of the yields or the inconvenience of using sealed tubes. Special objection to the use of phosphorus pentachloride was found in the violence of its action, and the tendency to form phosphorus-containing by-products. The trichloride and oxychloride, though less reactive, yield excessive quantities of these by-products which were found to be either phosphorus esters.[6] or the suboxide of phosphorus[7], the latter resulting from the action of the phosphorus chloride on the phosphorous acid first formed. Efforts to avoid these secondary actions, finally resulted in a very satisfactory method, the reaction being in the sense of the equation:

$$PCl_3 + ZnCl_2 + 3ROH = 3RCl + 2HCl + ZnHPO_3.$$

With proper precautions a 94 per cent. yield of propyl chloride was obtained:

Preparation of Propyl Chloride.—A zinc chloride solution, prepared by dissolving zinc in commercial hydrochloric acid, was evaporated until a thermometer in the liquid registered 240°. The hot mass (150 g.) was poured into a one-liter, round bottom Jena flask, and turned while cooling so as to leave exposed the maximum surface of solidified zinc chloride. The flask was placed upon a water bath and fitted with a suitable rubber stopper through which were adjusted two dropping funnels and a distilling column. One dropping funnel was arranged so as to admit phosphorus trichloride to the lowest level of the flask, while the other funnel dropped the alcohol upon the surface of the reaction-mixture. The distilling column, carrying a thermometer, was connected to an up-

[1] Jaraschinko, Chem. Centr., 1887, II, 334.

[2] Silver, Ber. 6, 35.

[3] Bull. soc. chim. (3), 1, 603 (1888).

[4] Aschan, Ber, 31, 1802; Berthelot, Ann. chim. phys.(3) 52, 97; Cahours, Jahresberichte, 1863, 524; Schorlemmer, Ann. 144, 187; Ann. 161, 268; Hudson, Am. Chem. J. 19, 245, 247.

[5] Berthelot, Ann. 127, 71; Würtz, Ann. chin. phys. (4) 3, 161; Saytzen, Ann. 179, 321, Pawlow, Ann. 196, 124; Kondakow, Russ. Ber. 28, 790; Scheschukow, Russ. Ber. 17, 509.

[6] Wurtz, Ann. 58, 72; Schiff, Ann. 103, 164; Menschutkin, Ann. 139, 343; Chambon, Jahresberichte, 1876, 205.

[7] Kraut, Ann. 158, 332; Pantier, Compt. rend. 76, 49; Risson, Compt. rend. 125, 1032.

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right coil-condenser into which water from a dropping funnel was admitted, so as to condense the gaseous hydrochloric acid evolved by the reaction; the end of the condenser was connected with an ordinary filter flask surrounded by ice water. When the apparatus was adjusted, one-half (150 g.) of the phosphorus trichloride was admitted to the flask and, while heating gently, one-third (90 g.) of the alcohol was admitted drop by drop. After this portion was added, the remainders of the phosphorus trichloride and the alcohol were admitted simultaneously and at equivalent rates; finally the water-bath was removed and the reaction-flask was heated with a constantly moving flame until the distillation was complete. The mixture of oil and water in the receiver was separated; the oil was dried with calcium chloride and distilled. From 270 g. of propyl alcohol were obtained 330 g. of propyl chloride, equal to 94 per cent. of the theoretical quantity.

This method of preparation of alkyl chlorides was next applied to isobutyl and isoamyl alcohols (See experiments 9 and 8 of table) but the yields were found to be only 60 per cent. and 75 per cent. respectively.

Since Grove[1] did not report clearly the yields obtained when he treated alcohols with zinc chloride and hydrochloric acid, it was decided to determine the relative merits of his and the above-described methods. In the case of isoamyl alcohol, after extracting the reaction-product with ether and then distilling, 37 per cent. of isoamyl chloride and 28 per cent. of other alkyl chlorides were obtained. Evidently Grove's method is conducive to secondary reactions, and the yields are quite unsatisfactory.

The method of Malbot[2] was next tried: propyl, isobutyl and isoamyl alcohols respectively were saturated with hydrochloric acid gas, mixed with an equal volume of fuming hydrochloric acid, sealed in tubes, and heated several hours at 100°-105°. The yields were equal to 82-85 per cent. of the theory. Since Malbot's reaction:

$$ROH + HCl \rightleftarrows RCl + H_2O.$$

is reversible by saponification, it can never become quantitative. This is confirmed by the following experiment. A mixture of equimolecular quantities of propyl chloride and water was heated for several hours at 100°-105°; the aqueous layer was found by titration to contain 16 per cent. of chlorine as hydrochloric acid, while the weight of the unchanged propyl chloride was 84 per cent.

Efforts were next made to improve the yields of these higher alkyl chlorides by modification of the phosphorus trichloride method employed with propyl alcohol. From consideration of it and the following experiments, the conclusions were finally drawn that maximum yields can be obtained and secondary reactions, as evidenced by the formation

[1] Ann. 174, 372.

[2] Bl. (13) 1 (603).

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of isomeric alkyl chlorides, alkylated phosphorus compounds and olefins, can be avoided: (1) when the gaseous hydrochloric acid of the distillate is completely absorbed by water, (2) when the phosphorus trichloride is brought into intimate contact with the zinc chloride and alcohol, (3) when the temperature of the reaction is elevated above the boiling point of the desired chloride and (4) when the zinc chloride is completely dissolved early in the reaction.

These and other points are illustrated in the following table of experiments:

Experiment	Alcohol Kind	Quantities taken for 3ROH PCl_3	Quantities taken for 3ROH $ZnCl_2$	Yields from Alcohol Desired RCl	Yields from Alcohol Total RCl	Yields from Alcohol Other Products	Flask Heated While Mixing	Observations and Remarks
1	A	1.8	1.8	63	74	8	Yes	ROH and $ZnCl_2$ in contact 18 hrs; uncondensed cases collected over H_2O.
2	A	3.0	3.0	49			Yes	The gaseous HCl was condensed.
3	A	5.3	2.6	16	36	41	Yes	Heated 2 hrs. under reflux before distilling.
4	A	1.0	1.3	46	56	15	No	Some $ZnCl_2$ remained undissolved.
5	P	1.5	1.0	74	74		Yes	PCl_3 added to $ZnCl_2$; then ROH dropped in; gaseous HCl condensed.
6	P	1.5	0.5	36	36		No	Mixture treated with water; oil dried and distilled; HCl condensed.
7	P	1.6	0.6	94	94		Yes	See page 1329.
8	A	1.5	0.3		75	0	Yes	No fraction above 105°; small quantity of tertiary RCl.
9	B	1.5	0.6		60	0	Yes	Some tertiary RCl.
10	A	1.5	0.5	68	88	0	Yes	See page 1332.
11	B	1.5	0.6		85	0	Yes	Same as experiment 10 but too much $ZnCl_2$ used.
12	A	1.0	3.0 $CaCl_2$	14	53		Yes	Heated under reflux for 2 hrs. before distilling.
13	A	1.0	1.0 $AlCl_3$		50	Yes	No	Large yields of high boiling products (200°+).
14	A	0.75	0.3 $AlCl_3$		60		No	Same as experiment 14.
15	P	1.0	1.0 Al ZnO	60		Yes	No	Some RCl carried off by the evolved hydrogen.
16	B	1.5	0.6		54		Yes	

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The kinds of alcohols indicated are isoamyl (A), normal propyl (P) and isobutyl (B). In all cases the calculation of quantities of materials had 3ROH as the basis; the yields, usually the result of one distillation, were calculated on the basis of the alcohol used.

A study of the above experiments shows that zinc chloride in the proportions of the equation:

$$3PCl_3 + 3ZnCl_2 + 6ROH = 6\,RCl + 6HCl + Zn_3(PO_3)_2$$

is excessive and, in fact, is positively injurious, depressing the yields and giving rise to higher-boiling condensation products. Therefore the reaction involved must be according to the equation:

$$PCl_3 + ZnCl_2 + 3ROH = ZnHPO_3 + 3RCl + 2HCl$$

or more probably (see experiment 7) is:

$$2PCl_3 + ZnCl_2 + 6ROH = Zn(HPO_3)_2 + 6RCl + 2HCl.$$

A comparison of experiments (1) and (4) shows that it is quite necessary to use an excess of phosphorus trichloride; owing to its volatility, some always escapes reaction.

The advantage of heating the mixture while adding the reagents is shown in experiments (6) and (7). The superiority of zinc chloride over the other condensing agents used is sufficiently indicated in the table. The use of calcium chloride is characterized by the formation of a preponderance of tertiary chloride; this behavior certainly merits further study. Aluminum chloride yielded quantities of high-boiling products whose composition was not determined.

Since, in his preparation of methyl and ethyl chlorides, Grove found that a concentrated solution of zinc chloride was as efficient as the fused solid, and, as was shown above, intimate contact of zinc chloride is of great advantage, this modification of the phosphorus trichloride method was tried with the higher alcohols.

Preparation of Isoamyl Chloride.—A 500 cc. round-bottom flask containing 90 grams of phosphorus trichloride was connected with the apparatus described under the preparation of propyl chloride. One of the dropping funnels held 132 grams of isoamyl alcohol; the other, 50 grams of warm zinc chloride solution (boiling 150°-160°). The alcohol was first dropped in as rapidly as possible while shaking the reaction-flask and warming gently; then the zinc chloride[1] was run in, care being exercised that its immediate solution was effected.

The mixture was distilled in the manner described above; the yield of washed and dried oil was 140 grams or 88 per cent. of the theory. One fractionation gave 16 grams boiling 80°-95° and 117 grams boiling 95°-105°—evidently some isomeric chloride was formed.

Preparation of Isobutyl Chloride.—In the same manner, with 222 grams

[1]Excess of zinc chloride should be avoided; when the evident reaction with the zinc chloride ceases, its further addition should be discontinued.

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of isobutyl alcohol, 204 grams of phosphorus trichloride and 92 grams of zinc chloride, a yield of 85 per cent. of washed and dried oil was obtained. In this experiment the quantity of zinc chloride used was somewhat excessive. Substituting liquid for solid zinc chloride and changing the manner of mixing the three substances as described above, while enhancing the yields with amyl and butyl alcohols, really depressed the yield with propyl alcohol; evidently the increased temperature of the reactions volatilized unchanged alcohol.

From consideration of all of the above experiments, the conclusion is drawn that *alkyl chlorides can be prepared with maximum yields by treating alcohols with phosphorus trichloride and anhydrous zinc chloride.*

The Mechanics of the ROH — PCl_3 — $ZnCl_2$ Reaction. It might superficially be supposed that the equation:

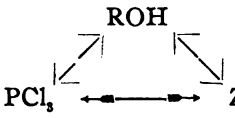
$$6ROH + 2PCl_3 = Zn(H_2PO_3)_2 + 6RCl + 2HCl$$

or, more in detail, the equations:

$$PCl_3 + 3ROH = H_3PO_3 + 3RCl$$
$$2H_3PO_3 + ZnCl_2 = Zn(H_2PO_3)_2 + 2HCl$$

sufficiently indicate the chemical mechanics involved; however, during the progress of the experiments it became more and more evident, that when these three substances are mutually brought into contact, *intermediate compounds are invariably formed.* Evidence for this view was seen in the following: When the reaction-product was treated with water and then extracted with ether (See experiment 6 and Grove's experiment, page 1330), a *stable oil* was obtained; on distilling, alkyl chloride and hydrochloric acid were given off, then at 102° a sudden violent decomposition took place, alkyl chloride and olefin were expelled and a white zinc and phosphate-containing solid separated. The hydrochloric acid, alkyl chloride, and olefin could not have been present in the oil, therefore these compounds must have been formed by the decomposition of some complex intermediate product.

Let us now consider the possibilities of the problem indicated in the diagram:



In the first place PCl_3 has no effect on $ZnCl_2$; ROH + $ZnCl_2$ gives at high temperatures[1] abundant yields of olefin, polmerized olefin and other compounds, but at low temperature, products indicated by ROH.$ZnCl_2$ or by the equation:[2]

$$ROH + ZnCl_2 = ROZnCl + HCl$$

Collateral evidence of the formation of these intermediate molecular

[1] Silva Jahresberichte 1873, 322; Nevoli, Bull.soc.chim. 24, 122; LeBel and Greene, Am. Chem. J. 2, 23; Balard, Ann. chim. phys. (3) 12, 320; Franklard, Ann. 74, 4; Wysch negradsky, Russ. Ber. 9, 192; Eltekow, do. 9, 222; Kondakow, do. 24, 113.

[2] Walter, J. pr. Chem. 59, 41.

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compounds may be deduced by considering the ease with which alcohols form addition-products with other metallic chlorides good examples of which for instance, are $SnCl_4.2C_2H_5OH$ and $SnCl_4.2C_2H_{11}OH$. When we treated stannic chloride with an excess of propyl alcohol we obtained no propyl chloride but a liquid boiling at 148°.

End-products of the $PCl_5 \leftarrow\!\!-\!\!-\!\!\rightarrow ROH$ combinations have already been mentioned; their intermediate products, theoretically considered, may be many; these intermediate products may give directly by heating or under the influence of zinc chloride and heat, the required alkyl chloride. A study of these intermediate products will be made.

URBANA, ILL.

ON THE COMBINING POWER OF CASEIN WITH CERTAIN ACIDS.

By J. H. LONG.

Received July 11, 1907.

In several recent papers I have shown the amount of different alkalies which may be combined with a given weight of casein to form salts,[1] and have also pointed out the behavior of hydrochloric acid in combining with the products of casein hydrolysis brought about by prolonged digestion in presence of pepsin, with subsequent heating.[2] These results suggested another line of enquiry, *viz*:—the combining behavior of the acid, without the aid of pepsin, at the ordinary temperature as well as at higher temperatures. The amount of acid combining at the ordinary temperatures may in many cases be found by simple titration, while for higher temperatures other means may be employed.

At the ordinary temperatures many dilute acids combine with casein as with other proteins to form salts, and the amount of acid so held is definite and constant. By warming, however, or by prolonged contact, the acids lead to the formation of hydrolysis products, some of which as amino acids, are strong enough to hold considerable quantities of the acids used as the combining and hydrolyzing agents. It was shown in the last papers quoted that the amount of hydrochloric acid held in this way is about what might be expected from the character of the amino acid groups probably developed. But in the present inquiry we are concerned with the activity of the acids when not assisted by the digesting power of the pepsin, and the first experiments were made with N/10 hydrochloric acid at the ordinary temperature, followed by some in which the combination was effected by heat.

Hydrochloric Acid.—A series of tests was made, using always 5 grams of pure casein prepared by the Hammarsten process and varying amounts of the weak acid, with water enough to make up always 100 cubic centimeters. The mixtures of weak acid and casein were allowed to stand

[1] This Journal, 27, 363; 28, 372.

[2] Ibid. 29, 223; 29, 295.

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about an hour with frequent shaking, and were then filtered, which, up to a certain strength of the acid, was readily possible. With stronger acid mixtures, however, a jelly-like mass was formed which could not be filtered rapidly or perfectly enough for the purpose.

When a filtrate could be secured, it was used for titrations with dimethylaminoazo benzene, phenol-phthalein and *p*-nitro-phenol, in most cases. Conductivity tests were frequently made on a part of the filtrate. In the mixtures which became too thick for filtration the whole was used for the titrations directly. The results obtained are shown in the following table, where the result of titrations with 25 cc. are reduced to 100 cc. for comparison:

TABLE 1.—5 GM. CASEIN + HCl.

CC. N/10 HCl	CC. Water	CC. N/10 NaOH. Orange	CC. N/10 NaOH. Phenol-phth	CC. N/10 NaOH. *p*-Nitro-phenol	Conductivity κ_{20}
5	95	0.0	2.8	2.4	0.000275
10	90	0.0	4.9	4.0	0.000445
15	85	0.0	12.0		0.000739
20	80	0.0	16.0		0.000946
..	..	..			
25	75	0.0	25.0	25.0	Jelly, titrated
30	70	0.0	30.0	30.0	whole mixture
35	65	trace	35.0	35.0	"
40	60	4+	40.0	40.0	"

It is evident from the table that the acid forms a soluble combination with the casein, and that for 5 gm. about 35 cc. of N/10 acid can be so held. With only 20 cc. of acid present, the mixture can be filtered. In the filtrate no "free" acid can be detected with the dimethylaminoazo benzene (which, in what follows, will be referred to as "orange"), but with phenolphthalein a large amount of alkali is required. This corresponds to combined acid and to the casein held with it also. The conductivity tests made on the filtrate show likewise a large amount of combined acid in solution. In titrating the jelly-like mixture, where more than 20 cc. of acid was used, the whole of this acid in combination may be recognized by aid of phenolphthalein, and with a fair degree of accuracy, too, if the titration is made quickly. The union of the combined acid with the added alkali is immediate and the reaction apparently becomes complete before combination of the liberated casein with further alkali begins. It follows therefore that a permanent color with phenolphthalein cannot be secured until the whole of the casein has gone into solution to form what I have described, in an earlier paper referred to as a "neutral" salt. This last reaction is somewhat slow, and it is possible to recognize rather easily when it begins. The reaction with the para nitro phenol is somewhat sharper here than is that with phenolphthalein.

In this reaction without the aid of heat 1 gm. of casein combines with about 7 cc. of N/10 HCl, or with about 25.5 mg. of the real acid. This combination is effected with the slightest possible conversion of the casein

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into smaller groups, and is doubtless due to the presence of the free amino groups of the casein itself. It is evident that a reaction at a higher temperature, accompanied by hydrolysis, would result in the combination of a much larger amount of acid because of the presence of *liberated* amino groups. This is shown in the experiments with the acid and pepsin already referred to, where about ten times as much acid as here found was combined. The combining power without the aid of pepsin was determined in a new set of experiments in which casein and dilute acid were mixed, evaporated on the water-bath, dried at 102°-105° and weighed. The residue was then ashed after addition of sodium carbonate and the chlorine found in the ash. In this series of experiments the constant weight of 1.87 gm. of anhydrous casein (2 gm. of air-dry casein) with increasing weights of acid used in N/10 strength, were taken in each case.

TABLE 2.—1.87 GM. CASEIN + HCl, HEATED.

Mg of HCl added	Increase in weight	HCl in dry residue	Water added, calc.
109.5	129.5	105.9	23.6
146.0	211.0	136.9	74.1
164.2	204.0	133.2	70.8
255.5	231.5	160.6	70.9
273.8	245.0	148.2	96.8
292.0	260.0	164.3	95.7
310.0	265.0	157.0	108.0
328.5	296.5	182.5	114.0
346.8	252.5	160.6	91.9
365.0	267.0	158.8	108.2

These results appear somewhat irregular, but this is doubtless due to the method of evaporation followed. They show, in general, that at the temperature employed casein will combine with about one-tenth its weight of hydrochloric acid. This seems to be the maximum value for the conditions of the test. It is perhaps better to say that casein and its hydrolysis products have this value. The water added is calculated from the difference in weight between the numbers of the second and third columns of the table and in the mean amounts to about two-thirds of the acid addition in the last six tests. In these tests the ratio of the acid to water added is 161.9:102.4, which is nearly in the proportion of 4 molecules of acid to 5 molecules of water. This water addition points to a comparatively advanced degree of hydrolysis.

Hydrobromic Acid.—The experience with hydrochloric acid suggested some similar tests with the analogous hydrobromic acid. A solution of this acid of N/10 strength was made and employed in the tests with a constant weight of casein, using in the titrations the "orange" indicator.

TABLE 3.—5 GM. CASEIN + HBr

CC. N/10 HBr	CC. H_2O	CC. N/10 NaOH. Orange
20	80	0.0
25	75	0.0
30	70	0.0
35	65	trace
40	60	6.0—

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It appears that slightly less than 35 cc. of the N/10 acid combines with the casein. On adding 40 cc. of acid and titrating back the reaction is not very sharp, but the addition of more than 5 cc. of alkali can be noted. This is in good agreement with the findings with the hydrochloric acid. To this last mixture phenolphthalein was added and then more alkali. The effect of the latter is to combine with the acid and then gradually dissolve the casein, which, by slight warming, may be accomplished in a short time. In this case, however, no heat was applied and an hour or more was required for complete solution. The N/10 sodium hydroxide was added in small portions as fast as the color disappeared through neutralization of the acid present and union with the acid group of the casein. The final permanent pink tinge from this indicator and the alkali was secured after the addition of nearly 86 cc. of the latter. As 40 cc. of N/10 alkali was used up in combining with the 40 cc. of N/10 hydrobromic acid added at the start, the remaining 46 cc. must have been used to combine with the casein. This is the amount practically required for 5 gm. of pure casein, as found by numerous previous experiments, and the test shows that in the hydrobromic acid combination there has been no essential change by hydrolysis to alter the combining proportions of the casein.

The combination of the casein with this acid forms a gelatinous, partly soluble mass which cannot be well filtered. The above tests were made therefore on the whole mixtures.

It was next attempted to find the amount of hydrobromic acid which combines with casein by aid of heat, applied during the evaporation of a solution in contact with the latter. In each case 1.87 gm. of pure casein was mixed with the acid in a small weighed porcelain dish and heated on the water-bath to complete dryness. The dishes were transferred to an air oven and heated half an hour to 102°-105° and weighed. The residues were ashed after addition of sodium carbonate and nitrate, and the bromine determined by the Volhard method. The following results were secured:

TABLE 4.—1.87 GM. CASEIN + HBr, HEATED.

Mg. of HBr added	Increase in weight	HBr in dry residue	Water added calc.
283.5	318.5	274.4	43.8
324.0	353.0	307.8	45.2
364.5	409.5	355.5	54.0
405.0	467.0	377.7	89.3
445.5	522.0	405.0	117.0
486.0	551.5	469.8	81.7
526.5	568.5	470.0	98.5
567.0	611.5	502.2	109.3
607.5	649.0	542.7	106.3
648.0	686.8	558.9	127.9
688.5	751.5	631.8	119.7
729.0	771.0	632.0	139.0
769.5	798.5	664.2	134.3
801.0	809.5	639.9	169.6

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Like the figures for the combination with hydrochloric acid the above are somewhat irregular. But they indicate a progressive addition of hydrobromic acid, amounting finally to about 35 per cent. of the weight of the pure casein. This very large increase in weight can follow, probably, only through partial hydrolysis and union with the resulting amino groups. In general, as indicated by the water addition shown in the last column, the extent of hydrolysis is much greater than with the corresponding reaction in which hydrochloric acid was used, although not as great as found for the latter combined with pepsin. No reason suggests itself for the greater activity of the hydrobromic acid.

Hydriodic Acid.—The experiments with this acid were carried out exactly as with the other halogen acids, but it was found that in the direct titration process the point at which no more acid combined with casein could not be as clearly recognized. When titrated by aid of methyl-orange and dimethylaminoazo benzene it was found that 1 gm. of pure dry casein combined with slightly less than 7 cc. N/10 HCl or HBr. The hydriodic acid is not as stable in aqueous solution as are the other acids and the traces of dissociation products from the casein seem to interfere somewhat with the delicacy of the end reaction in the titration. A number of experiments made, however, show that approximately 35 cc. of N/10 acid combine with 5 gm. of pure casein, which is the combining proportion of the other acids.

While the reaction at the ordinary temperature is not as sharp as in the other cases, that which follows by aid of heat appears to be about the same, as shown by the table which follows. In these experiments, as before, 1.87 gm. of dry casein was evaporated with increasing weights of N/10 hydriodic acid and the perfectly dry residue weighed. The combined iodine was then found in the ash of the fusion with sodium carbonate.

TABLE 5.—1.87 GM. CASEIN + HI, HEATED.

Mg. of HI added	Increase in weight	HI in dry residue	Water added. calc.
512	527.0	502.0	25.0
576	602.0	512.0	90.0
640	664.5	531.2	133.2
704	711.5	601.6	109.9
768	767.5		
832	857.0		
896	933.5	768.0	165.5
960	1013.5	870.4	143.1
1024	1086.5	921.6	164.9
1088	1135.5	857.6	277.9
1152	1223.0	966.4	256.6
1216	1269.5	1070.0	199.0
1280	1325.0	1075.0	250.0

While the numbers expressing the increase in weight are pretty regu-

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lar, those measuring the iodine added are not. The reason for this is not hard to give, however. The iodine was determined from a fusion process in which there was some loss, notwithstanding the presence of the sodium carbonate. The products before fusion are quite dark and hard, but may be ground down to a fine brownish powder. During the evaporation the mixtures present a gelatinous appearance, but not as marked as in the case of the hydrochloride. Some degree of solubility follows, and even the dried mass is partly soluble in water.

The product resembles very closely several medicinal preparations which have been placed on the market in recent years, but under names which suggest an origin other than from casein. This substance is undoubtedly the starting material in the manufacture of many of these compounds which are advertised to contain 20 to 25 per cent. of iodine. In the last of the combinations of the above table we have a content of over 33 per cent. of iodine as iodide. This probably does not represent the maximum combining power, but merely that corresponding to a certain degree of hydrolysis. It is interesting to note that the additions of hydrobromic and hydriodic acids are very nearly in molecular proportions.

Sulphuric Acid.—As distinguished from the halogen acid combinations those between sulphuric acid and casein are less soluble. While the halogen acids form compounds which behave like jellies the sulphuric acid compounds remain finely granular, and if stirred up with water soon deposit the apparently unchanged casein in a form easily separated by filtration. A series of mixtures was made as before and, after standing, the filtered supernatant liquid was used for titrations, 25 cc. being taken for each test. The results are reduced to 100 cc. for comparison.

TABLE 6.—5 GM. CASEIN + H_2SO_4

CC. N/10 H_2SO_4	CC. H_2O	CC. N/10 NaOH. Orange	CC. N/10 NaOH. Phenolphthalein	CC N/10 NaOH *p*-Nitrophenol	Cond. κ_{20}
5	95	0.0	1.2	0.8	0.000154
10	90	0.0	1.6	1.2	0.000184
20	80	0.0	2.6	2.0	0.000304
30	70	0.0	4.0	3.8	0.000666
40	60	4.4+	7.2	6.8	0.001737
50	50	13.0+	15.2	13.2	0.003759

The titrations with the "orange" show that a little over 7 cc. of N/10 H_2SO_4 must be used to neutralize 1 gm. of casein by this method, which result is essentially the same as found for the halogen acids. The values obtained with phenolphthalein and *p*-nitrophenol have the same meaning as with the halogen acids. They represent the acid combined with the casein which has gone into solution and also the casein itself, but as the reaction for the latter is not absolutely sharp, the values are somewhat irregular.

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The values given under the head of conductivity show also that the sulphate is not perfectly insoluble, but evidently much less soluble than the halogen compounds. This conductivity is not wholly due to the salt formed, however. On mixing 100 cc. of the distilled water used in all the experiments with 5 gm. of casein, and filtering through the Swedish filter papers employed in all the tests, a filtrate was secured which showed $\kappa_{20}=0.0000484$. The above result would have to be diminished by approximately this amount to find the true conductivity of the dissolved casein salt. The remainder is quite appreciable for the larger acid volumes used, because here much remains free.

No attempt was made to find the combining value of sulphuric acid at the higher temperature, because of the charring which follows on concentration.

Acetic Acid.—This acid forms a feeble combination with casein and unites approximately in the same proportion found for the other acids, as just described. It is well known that the destructive action of this acid on casein is far less than with the mineral acids, and advantage is taken of this in the preparation of pure casein by precipitation from milk.

A number of titrations were made as in the other cases using N/10 acetic acid with water, and 5 gm. of casein in each test. The mixtures were frequently shaken and filtered after an hour or more. As before the titrations were made on 25 cc., but the results are calculated to 100 cc.

TABLE 7.—5 GM. CASEIN + $HC_2H_3O_2$

CC. N/10 $HC_2H_3O_2$	CC. H_2O	CC. N/10 NaOH Orange	CC. N/10 NaOH Phenolphthalein	CC. N/10 NaOH *P*-nitro-phenol	Cond. κ_{20}
5	95	0.0	5.2	3.6	0.0000956
15	85	0.0	14.8	13.9	0.0001523
25	75	0.0	24.8	23.2	0.0001916
35	65	?	34.0	28.0	0.0002238
45	55	end not sharp	44.0	43.0	0.0002586

The acetic acid does not form a jelly with the casein, but behaves as does sulphuric acid. From the titration and conductivity values it is evident that a relatively large amount of the solid goes into solution. The titration values with phenolphthalein measure the alkali required to combine with the acid added, and also with the liberated casein, after being set free from the acid in the filtrate. About one-half of the alkali run into the first four filtrates, is used for each combination, since in titration the first drop of alkali added produces a turbidity. This turbidity increases and then disappears when enough alkali has been added to form first an acetate, and then the usual neutral salt with the casein, as shown by the permanent phenolphthalein color.

An attempt was made to find the increase in weight which follows on drying down a given weight of casein with the solution of acetic acid. The tests were carried out as in the other cases, but it was not possible

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to determine the combined acid in the dry residue, because of lack of delicacy in the method. The actual weight increase is given in the following table, the weighings being made after drying at 102-105°. The appearance of the dry residues suggested the formation of hydrolysis products similar to those secured in the other cases.

TABLE 8.—1.87 GM. CASEIN + $HC_2H_3O_2$, HEATED.

Mg. of $HC_2H_3O_2$ added.	Increase in Weight.
30	18.0
60	27.5
90	27.0
120	46.5
150	53.0
180	78.0
210	88.0
240	94.0
270	141.0
300	118.0

Oxalic and Tartaric Acids.—These acids combine with casein and form salts of rather marked solubility, but as the determination of the free acids in presence of the casein cannot be sharply made, the actual combining power was not found.

In the evaporation of mixtures of casein with these acids there is evidently considerable hydrolysis, and apparently combination with the acids. But on account of the non-volatility of the excess of acid used, it is not possible to fix very exact limits for the combination here.

Phosphoric Acid.—This acid in weak solution has a very marked action on casein. The combination forms a jelly almost immediately, and this dissolves in water to a considerable extent. The rapidity of jelly formation is even greater than with the halogen acids. On evaporation of such mixtures and drying at 105°, the increases in weight are in excess of the solid added in the form of phosphoric acid, pointing to a considerable fixation of water. Because of the lack of delicacy in the indicators, no satisfactory results were obtained in titrating the excess of acid left after mixing casein with the latter in the cold.

Boric Acid.—There appears to be no combination of this acid with casein. On mixing the latter with solutions of the acid, a separation soon follows, and the total amount of free acid seems to be found in the supernatant liquid. It was found, also, that after evaporating mixtures of casein with boric acid solutions the residue left contained, with the casein, free boric acid only, readily extracted with water and alcohol.

Behavior of p-Nitro-Phenol.—It will be observed that *p*-nitro-phenol was employed in a number of the above titrations, and that the results obtained through this indicator are, in most cases, similar to, but not quite identical with those found with phenolphthalein. The color

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change with the *p*-nitro-phenol is as rapid and as sharp as with the other in the mixtures titrated. It is evident, therefore, that in using this indicator, we are able to measure not only the free mineral acids, but the acid combined with casein also.

In the titration of the casein itself, considered as an acid, the range of the phenolphthalein is wider than that of the *p*-nitro-phenol, as illustrated by the results in the acetic acid experiments. This difference is possibly due to the fact that we have to deal with some decomposition products of casein in small amount, and the acid strength of some of these may not be sufficient to show with the *p*-nitro-phenol. This indicator may have practical value in differentiating between just such mixtures, but as yet its full importance cannot be assigned.

Conclusions.

These experiments show that the basic behavior of casein toward acid is as marked and definite as the acid behavior toward alkalies. At the ordinary temperature one gram of dry casein combines with nearly 7 cc. of N/10 hydrochloric, hydrobromic, hydriodic, sulphuric and acetic acids, and also with tartaric, phosphoric, oxalic and other acids for which numerical values could not be found. The base fixing-power is somewhat greater, as one gram combines with 9 cc. of N/10 sodium, potassium, lithium or ammonium hydroxide or carbonate.

With application of heat, as in the evaporation of weak acid solutions with casein, the combining power becomes much greater. For hydrochloric acid about four times as much acid appears to combine at the higher temperature as was found in the cold titration. For hydrobromic and hydriodic acids the combining rates at high temperature are relatively greater. This may be due to the simple effect of the heat in favoring the union with additional amino groups of the casein, but it is undoubtedly due, in part at least, to the formation of and combination with the products of hydrolysis.

My thanks are due to Mr. Frank Gephart, who rendered me much assistance in carrying out many of the above experiments.

NORTHWESTERN UNIVERSITY MEDICAL SCHOOL, Chicago, July, 1907.

STUDIES OF THE NITROGEN CONTENT OF WHEAT AND ITS DISTRIBUTION TO DIFFERENT PARTS OF AN INDIVIDUAL PLANT.

BY R. W. THATCHER AND H. R. WATKINS.

Received May 21, 1907.

The following article is a brief report of the results of a study of the distribution of nitrogen in the several parts of the different heads of wheat which grow from a single seed, and hence form a single individual wheat plant. The object of the study was two-fold ; first, what might be termed an anatomical study to show how the plant distributes its nitro-

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genous matter in the production and ripening of its seed; and second, to establish, if possible, a suitable basis for the selection of individuals of desirable characteristics to be used as seed in breeding up improved strains of wheat. The data obtained seem to afford conclusive evidence along both of these lines of investigation and are presented with these ideas in view. The studies involved a determination of the average weight of the kernels and their nitrogen content on about 350 single spikes (or heads) or parts of spikes of wheat. The full details of the results of all these determinations are to be published in a bulletin of this Station, and may be consulted there by any one who is interested in the matter. They are much too voluminous to be inserted in this brief article, and the analytical tables herewith presented contain only such averages and other individual data as are necessary to demonstrate the points in question.

In determining upon the proper basis of selection of desirable seed grain, the first point to be settled is as to which is the proper unit in such selection; the single kernel, the spike (or single head), or the whole plant (or "stool," as it is commonly called) which grows from a single individual seed grain. In the case of the single kernel, it is not possible, by any means yet devised, to measure accurately its chemical composition or the percentage of any desired constituent, such as nitrogen for example, without destroying the kernel, thereby rendering it unavailable for seed purposes. A great deal of investigation has been carried on with a view of definitely connecting the nitrogen content with some physical property of the kernel, such as size, weight, specific gravity, hardness, etc., etc. The results of these studies are discussed very comprehensively by Lyon in his historical summary of the investigations of the conditions affecting the composition and yield of wheat.[1] More recent investigations have been made by Snyder[2], Harper and Peter[3], and Soule and Vanatter.[4] The results of most of these investigations indicate that some idea of the relative nitrogen content of wheat kernels may be obtained from a measurement of some physical property and that a basis for selection of seed grain rich in nitrogen might be thus established. But unfortunately most of these investigations have resulted in associating high nitrogen content with some otherwise undesirable quality in seed grain. Furthermore, this method of selection does not permit one to judge as to whether the variations in nitrogen content between different kernels are likely to be due to hereditary influence or to environmental conditions during their growth, and hence

[1] "Improving the Quality of Wheat." Bulletin No. 78, B. P. I., U. S. D. A.
[2] Minn. Exp. Sta. Bull. No. 85 and No. 90.
[3] Ky. Exp. Sta. Bull. No. 113.
[4] Tenn. Exp. Sta. Bull. Vol. XVI., No. 4.

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leaves the question of their probable transmission to succeeding generations wholly undeterminable, except by actual experiment. Hence it has seemed to us that the selection of the individual kernels, while perhaps capable of giving some very valuable practical results, is not of sufficient accuracy to serve as the best basis for careful breeding for improvement in chemical composition. This leaves to be determined the question as to whether the spike or the whole plant is the proper unit. Several facts bearing on this point are demonstrated by the investigations recorded below, and are pointed out in the discussions of the several phases of the work.

The following lines of work were undertaken: (*a*) studies of the whole plant, including relation of nitrogen content to total weight of grain produced and to average weight of kernel; relation of composition of individual spikes to the length of straw; and the selection of a suitable sample for analysis to represent the remainder of the plant; and (*b*) studies of the distribution of nitrogen to kernels in different parts of individual spikes, including analyses of opposite rows of spikelets, of kernels from lower, middle and upper spikelets, and of grain from the outer and middle rows of kernels within the spikelets. It should be noted that all the plants used in this investigation were grown in rows and at equal distances apart in order to avoid as far as possible any differences due to unequal nutrition during growth.

Relation of Nitrogen Content to Weight of Kernel.

Lyon[1] has reached the conclusion that the percentage of proteid nitrogen in a wheat spike decreases as the average weight of the kernel, the average weight of proteid nitrogen in each kernel, and the total weight of nitrogen in the spike increases. Or in other words, that the spikes which show a high percentage of nitrogen contain lighter kernels and less actual weight of nitrogen. This conclusion was derived from the study of spikes of a single variety of wheat grown in a single field. It seemed to us to be desirable to determine whether the same rule should apply to other varieties of wheat and to wheats grown under different conditions, and whether the same law applies also to all the grain of a plant as well as to a single spike. For this purpose we selected thirty-seven different plants of wheat bearing a total of 212 spikes, representing five different varieties and grown at three different localities in this State, namely, the experiment station farm at Pullman, and two sub-stations at Ritzville and Quincy. Each individual spike was threshed separately and the number and weight of kernels, and their total nitrogen content determined. The data thus accumulated is far too voluminous to present in this article, but it may be stated that with only very infrequent exceptions (such as might be expected from unusual environmental con-

[1] Bureau of Plant Industry. Bull. 78, p. 57.

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ditions or experimental errors), the spikes showed the same phenomena observed by Lyon, namely, that high percentage of nitrogen in kernel is accompanied by low average weight of kernel and low total weight of nitrogen in the spike. The data concerning all the spikes of each plant were then assembled and averaged to give the information concerning the plants as a whole. These averages are presented in Table 1, which is given in full as it furnishes what are, so far as we are aware, the only analytical data of this kind which have yet been accumulated.

TABLE I.

RELATION OF WEIGHT OF KERNEL AND NITROGEN CONTENT OF ALL THE SPIKES OF DIFFERENT PLANTS.

				Average Composition of Spikes.				
Variety	Grown at	Plant No.	Number of Heads.	Number of Kernels.	Total Weight of Kernels. gms.	Average Weight of Kernels. gms.	Nitrogen in Kernels. mgms.	Nitrogen in Kernels. %
Bluestem	Ritzville	G	7	30	0.711	0.0225	20.84	3.009
"	"	F	6	29	0.750	0.0253	20.90	2.783
"	"	D	4	34	0.861	0.0254	22.85	2.656
"	"	E	6	41	1.100	0.0264	28.52	2.633
"	"	C	5	39	1.257	0.0314	30.80	2.474
"	"	B	5	36	1.160	0.0320	28.78	2.497
"	"	A	7	38	1.294	0.0340	29.14	2.254
Turkey Red	Pullman	B	20	27	0.554	0.0185	15.10	2.926
"	"	A	7	26	0.680	0.0230	18.49	2.830
"	Ritzville	C	4	30	0.430	0.0147	10.96	2.518
"	"	A	5	25	0.465	0.0185	11.74	2.517
"	"	B	5	30	0.749	0.0240	18.36	2.350
"	Quincy	C	5	25	0.740	0.0284	13.92	2.418
"	"	B	5	25	0.809	0.0316	16.79	2.089
"	"	D	5	22	0.685	0.0318	14.66	2.361
"	"	A	6	23	0.779	0.0343	15.82	2.046
Fife	Pullman	A	9	42	1.095	0.0253	29.90	2.858
"	Ritzville	C	5	49	1.398	0.0284	32.75	2.325
"	"	B	5	49	1.460	0.0294	33.72	2.313
"	"	D	5	56	1.690	0.0297	38.24	2.252
"	"	A	5	52	1.608	0.0304	38.13	2.417
"	Quincy	A	3	44	1.259	0.0277	25.59	2.113
"	"	C	6	47	1.699	0.0363	35.05	2.083
"	"	B	3	37	1.406	0.0366	31.32	2.261
Little Club	Ritzville	B	6	53	1.269	0.0233	38.02	3.010
"	"	A	7	54	1.414	0.0239	42.26	2.983
"	"	C	6	55	1.426	0.0254	42.30	2.982
"	"	D	6	53	1.512	0.0274	43.66	2.897
"	Pullman	B	9	43	0.938	0.0190	23.59	2.858
"	"	A	8	39	0.808	0.0196	21.95	2.900
"	"	C	5	47	1.098	0.0228	29.95	2.812
"	Quincy	C	4	41	1.277	0.0307	30.05	2.362
"	"	B	4	47	1.488	0.0310	23.69	2.301
"	"	A	4	46	1.494	0.0327	27.42	1.912
Forty-fold	Quincy	A	3	22	0.891	0.0399	18.25	2.095
"	"	B	4	26	1.168	0.0435	24.08	2.063
"	"	C	3	22	1.063	0.0474	18.46	1.756

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An inspection of this table, in which the plants of each variety and from the same locality are arranged in the order of the average weight of kernel, shows at once that the same law which has been found to hold for individual spikes applies as well to whole plants. The very obvious conclusion is that wheat plants which show by analysis a high percentage of nitrogen are those which bear a smaller total weight of grains, whose kernels are lighter in weight and whose total weight of nitrogen is less. It would seem, therefore, that the breeding of wheat of increased percentage of nitrogen is likely to involve a deterioration in other desirable qualities. Whether this be true, or whether the nitrogen percentage is a more strongly hereditary trait than the other properties, remains to be proved by experimental tests, which we are now inaugurating.

Composition of Opposite Rows of Spikelets of the Whole Plant.

As is well known by every one who has seen a wheat head, the spike is composed of two separate and distinct rows of spikelets growing on opposite sides of the stem. Lyon[1] having suggested as a result of his studies on a single variety of wheat that the analysis of one of these rows of spikelets from each of these spikes of the plant would serve as a measure of the nitrogen contents of the other half of the kernels, we desired to confirm the general applicability of this method of selection.

TABLE II.

COMPARISON OF OPPOSITE ROWS OF SPIKELETS (HALVES) OF ALL THE SPIKES OF A PLANT.

Variety	Number of Plants	Average Number of Heads per Plant.	Half	Average Composition of Each Half				
				Number of Kernels	Total Weight of Kernels gms.	Average Weight of Kernels gms.	Nitrogen in Kernels gms.	Nitrogen in Kernels %
Turkey Red	4	10	First	126	2.863	0.0238	0.0837	3.007
			Second	131	2.916	0.0231	0.0835	2.957
Fife.....	2	16	First	311	7.558	0.0240	0.2173	2.886
			Second	328	7.916	0.0238	0.2267	2.872
Little Club	5	12	First	251	5.638	0.0219	0.1536	2.752
			Second	250	5.650	0.0222	0.1536	2.748

The results of our work are presented in Table II, and show that the composition of one-half of all the heads of a plant is sufficiently accurate counterpart of the other half of the heads to serve as a basis of selection.

Relation of Composition of Individual Spikes to the Length of the Stem on Which They Grow.

A considerable variation in composition of different individual spikes of a plant having been often observed, we wished to ascertain what causes these differences. Individual heads usually grow upon stems of different lengths, the longest stem being presumably the one which started first and which received the most favorable nutrition during the growth of the

[1] Loc. cit. pp. 76-78.

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plant. We, therefore, selected several plants which showed straw (or stems) of quite variable lengths and separated and analyzed their spikes separately. The results from a few typical plants are presented in Table III. The other plants which were analyzed show the same general relationships, but the results of their analyses are omitted in order to shorten the table of analytical data.

TABLE III.

RELATION OF COMPOSITION OF DIFFERENT SPIKES OF A PLANT TO THE LENGTH OF STRAW.

			Composition of the Spike				
Variety	Head No.	Length of Straw	Number of Kernels	Total Weight of Kernels gms.	Average Weight of Kernels gms.	Nitrogen in Kernels gms.	Nitrogen in Kernels %
Turkey Red	1	18″	12	0.134	0.0112	4.493	3.353
	2	25″	21	0.369	0.0176	11.092	3.006
	3	30″	27	0.718	0.0266	20.217	2.815
	4	30″	28	0.720	0.0259	20.076	2.788
	5	33″	34	0.882	0.0271	23.868	2.706
	6	36″	34	0.864	0.0254	23.026	2.665
	7	39″	39	1.075	0.0276	26.676	2.481
Little Club	1	27″	18	0.192	0.0107	7.301	3.808
	2	27″	23	0.278	0.0121	9.266	3.333
	3	35″	32	0.576	0.0180	16.848	2.925
	4	35″	38	0.704	0.0185	19.936	2.832
	5	38″	42	0.994	0.0237	26.114	2.627
	6	39″	50	1.133	0.0266	28.781	2.540
	7	40″	57	1.362	0.0239	35.800	2.628
	8	41″	52	1.226	0.0240	31.590	2.578
Fife	1	24″	44	0.909	0.0206	28.220	3.104
	2	25″	28	0.446	0.0159	15.584	3.494
	3	31″	45	1.145	0.0254	30.888	2.955
	4	33″	35	0.784	0.0224	23.868	3.044
	5	34″	30	0.741	0.0247	21.902	2.955
	6	38″	42	1.262	0.0300	33.556	2.659
	7	40″	40	1.091	0.0273	27.518	2.522
	8	44″	66	1.963	0.0297	50.544	2.574
	9	44″	48	1.514	0.0315	36 083	2.383

These results clearly show that as the length of straw increases there is a quite regular increase in the number of kernels in the spike, the total and average weight of kernels and the total weight of nitrogen stored up in the spike, and an equally regular decrease in the percentage of nitrogen. This indicates that the differences between different spikes of the plant are chiefly due to differences in nutrition and other environmental conditions during growth and are not in any sense hereditary. This apparently eliminates the head or spike as a unit for selection for plant breeding purposes. It is further apparent from these results that those spikes which are richest in percentage of nitrogen are otherwise very poorly qualified to serve as seed for a new generation of plants.

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Another fact which appears in this table is that all the spikes of a plant which are of equal height have about the same composition, and that if we eliminate the abnormally short and abnormally tall stalks, the remaining spikes are fairly similar in composition. This would seem to be the true hereditary composition of the plant and a means of selection for plant breeding purposes.

Selection of One Spike to Represent Composition of Whole Plant.

The facts pointed out in the preceding paragraph made it appear possible that, since all the heads of the same plant of average normal height are fairly similar in character, one head might be selected and analyzed to give a knowledge of the other heads of the plant. Obviously this would be impossible in plants which contain many stalks of very irregular heights, but with plants in which the heads were all of similar growth it seemed very probable that such a system of sampling for analysis would be sufficiently accurate for purposes of selection. To test this several plants, of three different varieties, were taken and from each of these a single sample spike was selected and analyzed separately and the remaining spikes analyzed as a whole with the results as recorded in Table IV.

TABLE IV.

SELECTION OF ONE HEAD TO REPRESENT COMPOSITION OF PLANT.

Variety	Plant No.	Number of Heads.	Composition of Heads. Number of Kernels.	Total Weight of Kernels. gms.	Average Weight of Kernels. gm.	Nitrogen in Kernels. gm.	Nitrogen in Kernels. Per cent.
Turkey Red	G	One head	28	0.745	0.0266	0.0189	2.544
		Four "	132	3.644	0.0276	0.0918	2.521
Fife	B	One head	45	1.057	0.0235	0.0309	2.922
		Four "	161	3.653	0.0228	0.1031	2.821
"	E	One head	52	1.430	0.0275	0.0383	2.673
		Ten "	517	13.865	0.0269	0.3595	2.593
Little Club	I	One head	40	0.830	0.0208	0.0218	2.622
		Seven "	303	6.732	0.0221	0.1757	2.610
"	J	One head	41	1.140	0.0278	0.0296	2.600
		Four "	160	4.757	0.0297	0.1167	2.454
"	K	One head	41	0.915	0.0223	0.0263	2.870
		Seven "	271	5.710	0.0210	0.1678	2.939
"	L	One head	52	1.100	0.0212	0.0312	2.833
		Seven "	357	6.983	0.0190	0.2096	3.001

These results appear to show that such a method of sampling is quite satisfactory for purposes of selection. In most cases the agreement between the results on the two portions of each plant is as close as is usually expected of duplicate determinations. In one or two cases where the stalks were of quite irregular height the error is somewhat larger than might be quite desirable, but even in these cases no error in the selective rank of the plant is caused by the slight inaccuracy of representation of the

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plant by the sample head selected. We believe that this method of sampling for analysis for seed selection is preferable to that of Dr. Lyon (analysis of half of all the heads) in that it emphasizes the necessity for elimination of abnormal heads, and that it gives a means of selection which destroys a much smaller proportion of the kernels of the plant and leaves a correspondingly larger proportion to serve for purposes of propagation. We propose to use this method in practical experiments in breeding wheats both of high total nitrogen in the plant and of high percentages of nitrogen in the grain.

Distribution of Nitrogen to Different Parts of the Same Spike.

Having ascertained the laws governing the distribution of nitrogenous matter to the different spikes of the plant it seems desirable to discover whether there might be any regular variation in the distribution of the nitrogen to various parts of each individual spike. We first compared the composition of the kernels of the opposite rows of spikelets on several spikes from each of four different varieties of wheat. The full details of the results are omitted in order to economize space, but the maximum, minimum, and average variation in composition between the opposite rows of spikelets are presented in Table V.

TABLE V.

COMPARISON OF COMPOSITION OF OPPOSITE ROWS OF SPIKELETS ON THE SAME SPIKE.

Variety	Number of Spikes Examined.	Differences Between Composition of Opposite Rows of Spikelets. In Average Weight of Kernels. Maximum. gm.	Minimum. gm.	Average. gm.	In Per cent. of Nitrogen. Maximum. Per cent.	Minimum. Per cent.	Average Per cent.
Bluestem	7	0.0016	.0003	.0007	0.171	0.009	0.072
Fife	7	0.0013	.0002	.0005	0.173	0.023	0.081
Turkey Red	3	0.0009	.0002	.0003	0.066	0.035	0.050
Little Club	4	0.0022	.0001	.0009	0.151	0.027	0.069

These results show that the composition of the opposite rows of spikelets, or longitudinal halves, of a spike of wheat is practically identical. In most cases the differences found are not greater than might be expected from ordinary analytical errors. It is probable that even these differences might have been considerably reduced in some cases by rejecting the terminal spikelet, which does not properly belong to either row and which is very sensibly different in composition from other spikelets—as indicated in the following results. This latter fact was not discovered, however, until after the work on the composition of the opposite rows of spikelets was completed.

We next studied the variations in the composition of the grain from the upper and lower spikelets. A part of the sample spikes were divided into two sections, the upper and lower halves, while others were separated into three divisions, the upper, middle, and lower. The results of all the spikes of the same variety were averaged and are included in Table VI.

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TABLE VI.

COMPOSITION OF KERNELS IN SPIKELETS OF DIFFERENT PARTS OF THE SAME SPIKE.

Variety.	Number of Spikes Examined.	Average Weight of Kernel. Upper Spikelets. gm.	Middle Spikelets. gm.	Lower Spikelets. gm.	Composition of Kernels. Average Weight of Nitrogen in 1 Kernel. Upper Spikelets. mgm.	Middle Spikelets. mgms.	Lower Spikelets. mgm.	Average Per cent. of Nitrogen in Kernel. Upper Spikelets. per cent.	Middle Spikelets. per cent.	Lower Spikelets. per cent.
Bluestem	3	.0281	——	.0281	.697	——	.712	2.483	——	2.541
Fife	3	.0263	——	.0251	.674	——	.668	2.697	——	2.919
Little Club	3	.0208	——	.0220	.554	——	.623	2.538	——	2.683
Bluestem	4	.0358	.0365	.0364	.914	1.056	.998	2.568	2.762	2.720
Fife	2	.0252	.0272	.0255	.632	.736	.688	2.517	2.695	2.794
Forty-fold	2	.0368	.0397	.0359	.942	1.079	.999	2.542	2.744	2.812

These results show that the average weight of kernel is about the same in the upper and lower spikelets but somewhat higher in the middle spikelets of the same head. The kernels of the middle spikelets always contain the greater weight of nitrogen per kernel; and this was true not only the averages for each variety but of each single spike which we tested. The percentage of nitrogen shows a quite regular increase from the tip of the spike downward, every individual spike showing grain with the lowest percentage of nitrogen in the tips, and in all but three of the fourteen spikes, the highest percentage of nitrogen in the kernels from the lower division, the differences between the lower and middle spikelets being not so great, however, as between the middle and upper ones. From this it appears that the best kernels from the standpoint of composition are those growing in the middle of the spike.[1]

Finally, we separated the outer kernels from the middle kernels of each spikelet and analyzed separately all the grain from the outer and from the inner rows of kernels. The averages of the results on all the spikes of each variety are presented in Table VII.

TABLE VII.

COMPOSITION OF KERNELS FROM OUTER AND INNER ROWS IN THE SAME SPIKE.

Variety	Number of Spikes Examined.	Average Weight of Kernel. Outer gm.	Inner gm.	Composition of Kernels. Average Weight of Nitrogen in 1 Kernel. Outer mgm.	Inner mgm.	Average Per cent of Nitrogen. Outer per cent.	Inner per cent.
Little Club	4	0.0275	0.0223	0.767	0.667	2.653	2.848
Fife	3	0 0274	0.0245	0.744	0.639	2.684	2.618
Bluestem	4	0.0371	0.0318	0.987	0.841	2.732	2.538
Forty-fold	3	0.0303	0.0266	0.878	0.728	2.925	2.877

These results show clearly that the heaviest kernels containing the highest weight of nitrogen are invariably from the outer rows. Not only was this true in the average of each variety, but in every single spike which was tested. In general, the increase in nitrogen in the outer ker-

[1] Harper and Peter of the Kentucky Experiment Station found the same phenomenon in the case of a single head of Pootung wheat of which they analyzed each pair of spikelets separately. (See Ky. Sta. Bull. No. 113, p. 11).

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nels is greater than the increase in the weight of the kernels, resulting in a higher percentage of nitrogen, also, in the outer kernels, but there were frequent exceptions to this. It is apparent from these results that the kernels of the most desirable qualities came from the outer rows.

Briefly summarized, the results of our studies of the composition of the grain from different parts of a single head show that the best grains from the standpoint of weight of kernel, and nitrogen content, came from the outer grains of the spikelets in the middle of the spike. Whether these properties are capable of transmission to the succeeding generations can be determined only by experimental trial, which we are inaugurating.

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THE EFFECT OF COLORING MATTERS ON SOME OF THE DIGESTIVE ENZYMES[1].

By H. W. HOUGHTON.
Received May 29, 1907

The following investigation was conducted under the supervision of the Department of Chemistry of The George Washington University. I wish to express my indebtedness to Drs. C. E. Monroe and T. M. Price for their suggestions and assistance.

A search through the literature indicates that there has been but little work done in the study of the effect of coloring matters on the digestive enzymes. However, that which has been accomplished by H. A. Weber[2], Edward Gudeman[3], A. J. Winogradow[4], and others has given results which are exceedingly interesting and important.

In the article by H. A. Weber, it is shown that oroline yellow effects the peptic digestion of fibrin, while saffoline, magenta and methyl orange effect the pancreatic digestion of this body.

Gudeman found that ultramarine, burnt sienna, chrome yellow and ponceau effected the artificial peptic digestion of egg albumen when used in such quantities as one part, or less, of the color to 400 parts of the food.

In the investigation conducted by A. J. Winogradow, he found that Safranine, Ponceau R. R., Azofuchsine, G., Orange II, Coeruline S., Phoxine, R. B. N., Iodeosine, Chrysaniline, Magdala red, Azoflavine,

[1] Presented before the meeting of the American Chemical Society at Toronto, Ontario, June 27-29, 1907; being a thesis submitted to The George Washington University for the Degree of Master of Science.

[2] On the Behavior of Coal-tar Color toward the Process of Digestion, by H. A. Weber, Am. Ch. J., 1896, XVIII, 1092-1096.

[3] Artificial Digestion Experiments, by Edward Gudeman, J. Am. Chem. Soc. 1905.

[4] The Influence of certain Coal-tar Dyes on the Digestion, by A. J. Winogradow. Z. Nahr. Genussm., 1903, VI, 589-592.

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Benzopurpurine, and Cerise hindered the digestion of albumen by pepsin even when only a few milligrams of the colors were present; an amount corresponding to from 1:10 to 1:100 of the digestive solution. The action was almost inhibititive. The colors Quinoline yellow, Naphthylene green, Acid green, Iodine green, Acid azo-yellow T., Naphthol yellow, Aniline green, Primuline, Auramine O., Aniline orange, Martius yellow, and Metanil yellow interfered less than the first dyes, but in every case some effect was noticed.

As stated, in these experiments the investigator used his coloring matter in proportion from 1:10 to 1:100. This seems unpractical, as these colors are seldom used in such strengths in practice.

It was only after an extensive review of the work of these investigators that the following investigation was undertaken in order to ascertain the effect of other coloring matters which have not as yet been studied by artificial digestion.

In the investigations, the results of which are recorded herein, the effects of annatto, saffron, turmeric, cochineal, Bismarck brown and croceine scarlet 1-B were studied on the peptic digestion of fibrin, casein and egg albumen. There was also studied the effect of ground annatto seeds and oil yellow on the action of the fat decomposing enzyme, lipase, when it was mixed with butter fat. The experiments were carried out under laboratory conditions and it is not claimed that they represent exactly the conditions which exist in an animal, or that the phenomena would occur in precisely the same manner in an animal system, but it is believed that from a consideration of these results we may infer, with a fair degree of accuracy, what would occur in an animal system, if the bodies studied were introduced into it.

The Effects of Coloring Matters on the Digestive Enzyme, Pepsin.

The extent to which the fibrin, casein, and egg albumen, used in these experiments, were digested, was ascertained by determining the amount of nitrogen in solution and the amount remaining in the residues after the materials used had stood in contact with the active ferments for two hours. The nitrogen in all samples was determined by Gunning's method, which is one of the most accurate methods known at the present day.

Preparation of Materials Used. The fibrin[2], was obtained by whipping freshly drawn blood with a suitable instrument, the fibrin being deposited as an elastic, stringy material, which was freed from adhering corpuscles by thorough washing and kneading. Fibrin, so obtained, is

[1] Gunning's Method for Nitrogen, Official Methods of Analysis, A. O. A. C. Bulletin 46, Bureau of Chemistry.

[2] Physiological Chemistry, by Charles E. Simon, M. D. Hand Book for Bio-Chemical Laboratory, by John A. Mandel.

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still contaminated with serum-globulin and certain phosphorus-containing substances which have resulted from the decomposition of leucocytes. This serum-globulin was removed by separate washing and kneading in a 5 per cent. solution of common salt. Then when the fibrin had been further freed from sodium chloride it was extracted with alcohol and then with ether and finally preserved in a solution of equal parts of glycerol and water.

The casein was prepared by diluting 400 cc. of fat-free milk with four times its volume of water and acidifying with acetic acid to the extent of 0.75–1.0 pro mille. It was washed free of acid by decantation, filtered, shaken with anhydrous ether, again filtered and dried in a vacuum desiccator. After drying, it was pulverized and passed through a one millimeter sieve.

The egg albumen was obtained from fresh eggs by boiling them until the whites were hard. The coagulated whites were separated from the yolks and ground in a mortar, first with 95 per cent. alcohol, then with anhydrous ether. The ether was filtered off and the mass of coagulated egg albumen was placed in a vacuum desiccator and dried.

The annatto, saffron, turmeric and cochineal were prepared by placing a quantity of each coloring matter on a filter and treating each separately with boiled distilled water until practically the entire amount of the soluble coloring matter present had been extracted. This method required about a week for each coloring matter. Each of these extracts was evaporated to dryness and powdered. By this means the author avoided using material which was useless as coloring matter.

Mode of Procedure. In order to shorten the work so as to make it possible to handle the entire series of experiments on each substance at the same time it was found advantageous to use one half of a gram of the protein. This allowed the manipulator the opportunity to wash thoroughly each residue and still not have too large a volume of filtrate to handle.

The first protein studied in this series of experiments was fibrin, which is one of the constituents of meat and meat products. Thus it is of interest to obtain some data as to the effect of these coloring matters on products which are eaten by man. These experiments were conducted under the most favorable conditions, and in order that there should be a uniformity of results, each series of experiments was completed at the same time, thus avoiding the possibility of having a slight lowering or rising of temperature in the different members of the series that would tend to decrease or increase the digestibility to a slight extent, for if this occurred it would be impossible to draw conclusions as to whether or not one coloring matter was more active than another.

Effect of Coloring Matters on the Peptic Digestion of Fibrin. The fibrin

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was taken from the preserving fluid, placed on a filter and washed thoroughly with boiling distilled water until free from glycerol. Then it was placed in an oven and dried at 115°. When dried so that it could be handled, duplicate samples, 0.5 gram each, were weighed out for the total nitrogen determination. The remaining samples of 0.5 gram each were weighed out in Erlenmeyer flasks. In these respective flasks varying amounts of coloring matters were placed as shown in the table. After all the flasks were properly numbered and contained the desired constituents, fifty cubic centimeters of artificial gastric juice[1] were added and in each case the temperature was brought to 40°. Then they were placed in an incubator and kept at 40° for two hours, when they were removed and brought to a boil at once. They were immediately filtered and washed with boiled distilled water until the filtrates were no longer colored. When this stage was reached the respective residues of the samples were placed in properly labeled Kjeldahl flasks and the nitrogen determined.

The accompanying table will demonstrate the effect of some of the coloring matters used in different amounts of artificial gastric juice.

Fibrin	Per Cent. of Digestibility					
Ratio used.....	0	1:100	1:200	1:400	1:800	1:1600
Annatto.....	96.2	96.2	95.8	95.9	96.2	96.2
Saffron.....	56.2	85.9	94.7	96.2	96.2	96.2
Turmeric.....	96.2	61.2	69.2	80.3	94.0	96.2
Cochineal	96.2	56.4	96.1	95.7	96.2	96.2
Bismarck Brown...	96.2	48.6	85.6	88.1	92.8	95.6
Croceine Scarlet 1-B	96.2	0.0	0.0	0.0	0.0	0.0

In this work the total amount of digested nitrogen in the filtrate was only determined where there was a considerable decrease in the per cent. of digestibility due to coloring matter. This was done to show that the determination of the digestibility of the substance can be made by determining it indirectly from the undigested nitrogen in the residue or by determining it directly from the digested nitrogen in the filtrate. As these two percentages of digestibility were approximately equal, the conclusion can readily be drawn that the determination of digestibility from the undigested nitrogen in the residue is just as accurate as the determination of the digestibility from the digested nitrogen in the filtrate.

The annatto when added to fibrin has no effect on the enzymic activity in any case.

The saffron, when in proportions of 1:100 diminishes the enzymic activity on fibrin, but it is seldom used in such a strength. When used in smaller quantities it is without effect.

The turmeric diminishes the enzymic activity when used in proportions

[1] Prepared by adding 10 mg. of pepsin to 50 cc. of a 0.2 per cent. solution of hydrochloric acid.

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of 1:100, 1:200 and 1:400, while in the proportions of 1:800 and 1:1600, it is practically without effect.

The cochineal diminishes the enzymic activity when used in proportion of 1:100, but this strength is seldom used. Smaller quantities have no effect.

The Bismarck brown diminishes the enzymic activity in proportions of 1:100 and 1:200, but these are not practical, as the colors are too strong. Smaller quantities produce no effect.

The croceine scarlet 1-B stops the digestion of fibrin entirely. As it was seen by the determination of nitrogen in the residue that the fibrin absorbed some of the coloring matter and that none of the substance was digested, it is, therefore, fair to conclude that this coal-tar dye prevents the enzymic activity.

In practice the coal-tar dyes[1] are replacing the animal and vegetable coloring matters, for instance, croceine scarlet is replacing cochineal and the azo yellows are replacing vegetable coloring matters in butter.

Effect of Coloring Matters on the Peptic Digestion of Casein.—The 0.5 gram samples were weighed out in this series of experiments and digested in the same manner as with the fibrin. In each case the coloring matter was weighed out in the proportions as shown in the table.

Casein.	Per cent. of Digestibility.				
Ratio used 0	1:100	1:200	1:400	1:800	1:1600
Annato.....98.2	66.3	87.3	96.8	96.8	98.2
Saffron.....98.2	78.3	78.8	90.1	97.0	97.8
Turmeric.....98.2	31.6	73.2	79.0	87.1	87.2
Cochineal 98.2	71.8	86.1	87.3	98.1	98.1
Bismarck Brown...98.2	58.9	98.1	98.1	98.1	98.2
CroceineScarlet,1-B 98.2	0.0	0.0	18.7	56.6	70.0

From the results in this table it can be said that the coloring matters which appear to affect the peptic digestion of casein are saffron, turmeric, cochineal and croceine scarlet 1-B, but cochineal and saffron may be exempted from this classification, as these coloring matters are very seldom used in the proportion of 1:400, or larger, and in smaller proportions they have no effect on the enzymic activity.

Effect of Coloring Matters on the Peptic Digestion of Egg Albumen.—The same mode of procedure was followed with egg albumen as with fibrin and casein, as will be seen by the accompanying table.

Egg Albumen.	Per cent. of Digestibility.				
Ratio used 0	1:100	1:200	1:400	1:800	1:1600
Annatto.....54.0	30.8	47.1	47.0	46.9	47.3
Saffron.....54.0	15.0	34.8	36.6	50.9	53.4
Turmeric.....54.0	1.89	8.03	29.0	37.7	39.7
Cochineal 54.0	11.1	30.4	39.6	41.3	42.4
Bismarck Brown....54.0	10.6	27.5	30.3	30.3	33.3
Croceine Scarlet, 1-B 54.0	0.0	0.0	0.0	6.36	19.7

[1] The Scientific Development of the Coal-tar Color Industry, by Professor R. Meldola, R. C. S., F. I. C., J. Soc. Dyers Colorists, 1886.

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The saffron is without effect except when it is used in the proportions of 1:100, 1:200 and 1:400.

The annatto, turmeric, cochineal, Bismarck brown and croceine scarlet 1-B diminish the enzymic activity in every case.

Conclusions.

From the study of the tables the following general conclusions may be drawn in regard to the effect of annatto, saffron, turmeric, cochineal, Bismarck brown and croceine scarlet 1-B, on the activity of peptic digestion of fibrin, casein and egg albumen:

(1) Annatto, when used in the given proportions, is without effect on the enzymic activity on fibrin while it diminishes the enzymic activity on egg albumen and casein.

(2) Saffron diminishes the enzymic activity on fibrin, casein and egg albumen when used in proportions varying from 1:100 to 1:400, while smaller quantities have no effect.

(3) Turmeric has no effect on the enzymic activity on fibrin when used in proportions of 1:800 or smaller, while with casein and egg albumen it diminishes the enzymic activity in each case.

(4) Cochineal and Bismarck brown diminish the enzymic activity on fibrin and casein when used in proportions varying from 1:100 to 1:400, while with egg albumen the enzymic activity is diminished throughout.

(5) Croceine scarlet 1-B prevents entirely the enzymic activity on fibrin, while with casein and egg albumen the enzymic activity is prevented when proportions of 1:100 to 1:200 are used. Smaller quantities of the same dye diminish the enzymic activity on casein and egg albumen.

Effect of Coloring Matters on the Hydrolysis of Butter Fat by Lipase.

Before giving the description of this series of experiments it will be of interest to refer to the relation of lipase to fat metabolism. The reversible action of lipase furnishes an explanation of fat absorption. Lipase is found in all tissues of the body that have been tested, notably in the liver, active mammary gland, blood, lymph and intestinal mucosa. The storing and translocation of fats may be called "lipogenesis," the process being analagous to "glycogenesis." Both phases of lipogenesis may be brought about by the enzyme, lipase, which is either fat forming or fat splitting, according to conditions.

Preparation of Materials Used.—The lipase was prepared from calf liver in the following manner:[1] Fifty grams of freshly chopped liver were weighed out and ground thoroughly in a mortar with water and sand until well macerated. The mass was allowed to digest at 40° C. for one day. It was then filtered and made up to 100 cc. so as to have a

[1] Concerning Lipase, the fat-splitting enzyme, and the reversibility of its action, by J. H. Kastle and A. S. Loevenhart, Am. Ch. J., 24, 491-525, 1900.

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50 per cent. solution. A little chloroform and sodium carbonate were added to the solution so as to preserve its activity.

The butter fat was prepared from double cream by extracting the fat with anhydrous ether to which a little sodium carbonate had been added.

Mode of Procedure.—The first efforts were directed toward ascertaining the proportions in which each of the two coloring matters, annatto seed and oil yellow, were used for coloring butter. This was arrived at by mixing the coloring matters with lard in various proportions. With annatto seeds it was found that a good butter color can be obtained between the proportions of 1:500 to 1:1000. With oil yellow it was found that a good color can be obtained between 1:1000 to 1:10000. These proportions are not precisely used in practice for coloring butter, as this fat has very often a natural color, but if these colors when used in the given proportions do not affect the hydrolysis of the butter fat, they will not when used in smaller quantities.

In these experiments the intermediate proportions between these ratios were used. In each case one gram of the neutral butter fat was weighed out and the varying amounts of the coloring matters were added, as may be seen in the tables.

BUTTER FAT AND ANNÀTTO SEEDS.

Proportions used	0	1:500	1:1000	1:2000
Amount of butter fat used (grams)	1	1	1	1
Amount of annatto used (grams)	0.0	0.002	0.001	0.0005
Amount of lipase solution used (cc.)	2	2	2	2
Amount of water used (cc.)	10	10	10	10
Length of digestion (hours)	7	7	7	7
Amount of N/20 HCl used (cc.)	0	0	0	0
Amount of N/20 NaOH used (cc.)	0.4	0.5	1.5	1.6

BUTTER FAT AND OIL YELLOW.

Proportions used	0	1:1000	1:2000	1:5000	1:10000
Amount of butter fat used (grams)	1	1	1	1	1
Amount of oil yellow used (grams)	0.0	0.001	0.0005	0.0002	0.0001
Amount of lipase solution used (cc.)	2	2	2	2	2
Amount of water used (cc.)	10	10	10	10	10
Length of digestion (hours)	6	6	6	6	6
Amount of N/20 HCl used (cc.)	0	0	0	0	0
Amount of N/20 NaOH used (cc.)	0.5	1.8	1.2	1.0	1.0

Conclusions.

From the results shown in the tables it may be seen that there were no retarding effects caused by the coloring matters, annatto or oil yellow. As a matter of fact, each one aided the hydrolysis of the butter fat. There is no explanation to give for this increase of hydrolysis of the butter fat except that it might be suggested that the coloring matters contain some free acid. But this is not justified, as checks were made in each case. The only reason that can be given is that the coloring matters contain some lipolytically active substance as a part of their composition.[1]

[1] On the Action of Lipase, by Alonzo E. Taylor, J. Biol. Chem., 8, 87-104, 1906.

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LOSSES OF AMMONIA FROM CULTURE SOLUTIONS.

By Jacob G. Lipman and Percy E. Brown.

Received May 17, 1907.

The isolation of pure cultures of nitrous and nitric ferments baffled for a long time the efforts of many bacteriologists. It was reserved for Winogradski[1] to offer a brilliant solution of the difficult problem, and to demonstrate that the isolation of these organisms may be accomplished with comparative ease where the proper culture methods are employed. Our knowledge of such culture methods has been amplified further by Omelianski[2] who has proposed the following culture solution for the preparation of crude cultures of the nitrous ferments:

Ammonium sulphate	2 gms.
Sodium chloride	2 "
Potassium phosphate	1 "
Magnesium sulphate	0.5 "
Ferric sulphate	0.4 "
Distilled water	1000 cc.

To each 100 cc. of this solution there is to be added 1 gm. of magnesium carbonate, which is to serve as the base for neutralizing the nitrous and nitric acid formed in the oxidation of the ammonia.

The same solution has also been employed for the systematic study of the nitrifying power of different soils, or of the same soil under different conditions of treatment. Remy[3] who was the first to propose such systematic investigations of the various bacteriological functions of soils inoculated measured portions of this culture solution, and by means of qualitative tests noted the rate at which the ammonia reaction disappeared, and the nitrite and nitrate reactions became more intense. The same, or a similar procedure was followed by Wohltman, Fischer, and Schneider[4], and Ehrenberg[5]. Löhnis[6] found the addition of magnesium carbonate impracticable for the quantitative study of nitrification, because of the very considerable losses of ammonia from the culture solutions. He employed, instead, calcium carbonate with solutions containing only one gm. of ammonium sulphate per liter.

It was noted in our own studies on the nitrifying power of various soils that the ammonium sulphate culture solutions prepared according to the directions of Omelianski, lost large quantities of ammonia. In order to secure more exact data as to the extent of these losses we prepared one liter of the ammonium sulphate culture solution, and distrib-

[1] Ann. inst. Pasteur., Vol. 4, 1890, No. 4; Ibid, vol. 5, 1891, No. 2.
[2] Centr. Bakt. Parasitenk., II, 5, 539, (1899).
[3] Ibid, 8, 657, (1902).
[4] Ibid, 12, 304, (1904).
[5] Landw. J., 33, 1, (1904).
[6] Centr. Bakt. Parasitenk., II, 13, 709, (1904).

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uted it in 100 cc. portions in round flat-bottomed Jena flasks. Eight of the ten flasks were sterilized in the autoclave at two atmospheres of pressure, while two were left unsterilized. Immediately after sterilization ammonia determinations were made in two of the sterilized portions of the solution, and likewise in the two unsterilized portions. The six remaining portions were placed in the incubator at 28° C., and two of these analysed for ammonia at the end of six days, twelve days and twenty-four days, respectively. The following table shows the amount of ammonia found in each case:

NITROGEN AS AMMONIA IN THE CULTURE SOLUTIONS.

Analysed Immediately	Unsterilized.... 43.45 mg.	Average 43.45 mg.	
	" 43.45 "		
	Sterilized..... 36.82 "	" 36.99 "	
	" 37.16 "		
At the end of six days.	" 27.26 "	" 27.17 "	
	" 27.09 "		
At the end of twelve days.	" 24.23 "	" 24.40 "	
	" 24.58 "		
At the end of twenty-four days.	" 17.57 "	" 17.44 "	
	" 17.31 "		

The figures in this table show clearly that the losses of ammonia from the Omelianski culture solutions may be very large. It is evident that considerable amounts of it are lost during sterilization in the autoclave, for we note that the sterilized portions contained, on the average, 36.99 mg. of nitrogen as against 43.45 mg. in the unsterilized portions. Further losses of ammonia occurred in the sterilized portions, when they were allowed to stand for longer or shorter intervals. Thus at the end of six days the sterilized portions contained on the average 27.17 mg. of nitrogen; at the end of twelve days 24.40 mg., and at the end of twenty-four days only 17.44 mg. In other words, almost three-fifths of the entire amount of ammonia present in the fresh culture solution were lost in the course of twenty-four days.

Another series of culture solutions was prepared partly to check the foregoing results and partly to furnish information as to the losses in sterilized and inoculated solutions. Twenty 100 cc. portions of the Omelianski culture solution were prepared in the usual manner with the single difference that calcium carbonate was used instead of magnesium carbonate in ten of these portions. All but four of the twenty portions were sterilized in the autoclave, and ammonia determined in four of the sterilized portions, as well as in the four unsterilized portions. The following amounts of ammonia nitrogen were found:

Unsterilized		Sterilized	
$MgCO_3$	No. 1—40.03 mg. No. 3—40.20 "	$MgCO_3$	No. 5—34.84 mg. No. 7—34.92 "
$CaCO_3$	No. 2—41.07 " No. 4—40.72 "	$CaCO_3$	No. 6—40.55 " No. 8—40.37 "

We note here that in the portions supplied with magnesium carbonate

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there was a distinct loss in the sterilized solutions as compared with the unsterilized portions. It seems, furthermore, that there was a slight loss even in the unsterilized portions provided with magnesium carbonate; for the yields in culture solutions 1 and 3 were 40.03 mg. and 40.20 mg., respectively, as against 41.07 mg. and 40.72 mg. for the corresponding solutions 2 and 4, where calcium carbonate was employed. Moreover, the losses of ammonia from the sterilized portions supplied with calcium carbonate were quite slight when compared with those in the corresponding solutions supplied with magnesium carbonate.

The remaining 12 sterilized portions of the culture solution were placed in the incubator and four of them analysed at the end of six days, four at the end of 12 days, and the last four at the end of 25 days. Six of these solutions were each inoculated after sterilization with 10 cc. of soil infusion equivalent to 5 gms. of soil. The following amounts of ammonia nitrogen, and, in the inoculated portions, also of nitrite and nitrate nitrogen, were found in the several solutions.

IN SIX DAYS.

		Ammonia Nitrogen.	Average	Nitrite Nitrogen	Nitrate Nitrogen
$MgCO_3$	Sterile—	No. 9—31.63 mg.	30.63 mg.	0.19 mg.	0.062 mg.
	Inoculated—	No. 11—29.64 mg.			
$CaCO_3$	Sterile—	No. 10—39.60 mg.	39.73 mg.	0.15 mg.	0.089 mg.
	Inoculated—	No. 12—39.86 mg.			

Comparing the amounts of nitrogen found at the end of six days with those found in the corresponding fresh solutions, we note further losses. The latter are greater in the portions containing magnesium carbonate, and are slight, but none the less distinct, in the portions containing calcium carbonate. In the inoculated culture solutions 11 and 12, small quantities of nitrite nitrogen were already present at the end of six days.

IN TWELVE DAYS.

			Ammonia Nitrogen.	Average	Nitrite Nitrogen.	Nitrate Nitrogen.
$MgCO_3$	Sterile—	No. 13—	22.96 mg.	23.30 mg.	0.06 mg.	0.078 mg.
	Inoculated—	15—	23.65 mg.			
$CaCO_3$	Sterile—	14—	38.83 mg.	37.23 mg.	0.30 mg.	0.250 mg.
	Inoculated—	16—	35.64 mg.			

At the end of twelve days the losses in the magnesium carbonate solutions had become much greater. Only 23.30 mg. of ammonia nitrogen remained, on the average, in these solutions. The inoculated portion 15 showed scarcely any nitrite and nitrate, indicating thus that the process of nitrification had not yet become active. In culture solutions 14 and 16, where calcium carbonate was used, small but distinct losses occurred. In the inoculated solution 16, the loss was greater than that in the corresponding uninoculated solution 14, a loss which was but partly accounted for by the nitrite and nitrate nitrogen found. It should be noted here, also, that in the inoculated solution 16 the amounts of nitrite and

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nitrate nitrogen were 0.30 mg. and 0.25 mg., respectively, as against 0.15 mg. and 0.089 mg. in the corresponding solution 12 at the end of twelve days. The nitrification process had evidently made some headway in the intervening six days, where calcium carbonate was used, but not in the solutions where magnesium carbonate was used.

IN TWENTY-FIVE DAYS.

		Ammonia Nitrogen.	Nitrite Nitrogen.	Nitrate Nitrogen.
$MgCO_3$	No. 17 Sterile —	18.64 mg.	0.15 mg.	0.025 mg.
	19 Inoculated —	18.04 mg.		
$CaCO_3$	18 Sterile—	35.56 mg.	1.74 mg.	1.000 mg.
	20 Inoculated —	22.52 mg.		

A still further loss of ammonia occurred in solutions 17 and 19, containing magnesium carbonate. The second of these, which was inoculated with soil infusion, showed the greater loss without corresponding increase in the amount of nitrite and nitrate nitrogen. On the other hand, the solutions containing calcium carbonate not only suffered smaller losses of ammonia, but showed active nitrification in the inoculated portion. We note, thus, that at the end of twenty-five days the magnesium carbonate solutions had lost considerably more than one half of the ammonia nitrogen which they originally contained, whereas the calcium carbonate solutions lost scarcely more than one-eighth of the initial amount. In the inoculated portion, supplied with calcium carbonate, the amount of ammonia nitrogen found at the end of twenty-five days was only 22.52 mg., as compared with the 35.56 mg. found in the corresponding sterile portion. We find, at the same time, that a portion of the ammonia nitrogen which had disappeared from the inoculated portion had been converted into nitrite and nitrate nitrogen to the amount of 1.74 mg. and 1.00 mg. respectively. The quantity of nitrite and nitrate nitrogen thus recovered is not sufficient to account for the greater loss of ammonia from the inoculated solution. The discrepancy observed here would tend to support the claim made by Godlewski[1] and others that gaseous nitrogen may be liberated in the nitrification of ammonia. Godlewski attributes this loss not to the respiration processes of the bacteria themselves, but to the reaction between nitrous acid and ammonia.

$$NH_3 + HNO_2 = 2H_2O + N_2.$$

It is to be added here that the formation of nitrite and nitrate may proceed simultaneously even where large quantities of ammonia are still present in the culture solution. Winogradski and Omelianski point out[2] that the nitrate ferments are very susceptible to ammonia and do not show any appreciable activity until nearly all of it had been converted into nitrite. Their results were secured with solutions containing mag-

[1] Centr. Bakt. Parasitenk., II, 2, 458, (1896).

[2] Ibid, 5, 439, (1899).

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nesium carbonate, and find strong support in observations made elsewhere. Where calcium carbonate instead of magnesium carbonate is present in the culture solutions, the process of nitrification is modified, and the presence of unoxidized ammonia does not seem to inhibit the development of the nitric ferments. Under actual soil conditions the formation of nitrites and nitrates may not only occur at the same time, but the nitrites may be oxidized as fast as they are formed, and the activity of the nitrous ferments may thus be concealed. It should be noted here, however, that organisms may exist in the soil, which have the power of converting ammonia directly into nitrate without the intermediate formation of nitrites. Such, at least, is the claim made by Kaserer,[1] and there are observations made by others, which would lend support to this claim.

NEW JERSEY EXPERIMENT STATIONS,
New Brunswick, N. J.

THE FLUORINE CONTENT OF MALT LIQUORS.

BY A. G. WOODMAN AND H. P. TALBOT.
Received July 3d, 1907.

In a previous paper[2] the authors outlined a method for the approximate estimation of fluorides when present in minute quantities, such as might occur in food products. At that time the hope was expressed that it might be possible to examine by means of the method, various classes of food products with a view to determining the limiting values for their fluorine content. For obvious reasons, malt liquors seemed excellent material for beginning such an investigation, and it is the purpose of the present paper to summarize the results obtained in the examination of a number of the brands of malt liquor on the market, as well as the materials used in brewing.

Method.—The method used was similar to that already described, except that on account of the large amounts of carbonic acid in the beers, it was found necessary in every case to add a somewhat greater quantity of barium acetate, enough being used to ensure an excess in the filtrate from the barium sulphate and fluoride. For the same reason more sulphuric acid (3-4 cubic centimeters instead of 2-3 as previously directed) is necessary during the etching. An insufficient amount of either of these would occasion negative results, even if an appreciable amount of fluoride were present.

In extracting the fluoride from malts and barleys it was found inadvisable to grind the sample and extract with hot water, as would be done in the brewery operation of mashing, because the large amount of sugary and starchy matters extracted interfere with the subsequent precipitation of the fluoride. Satisfactory results were obtained in the case of malt by

[1] Centr. Bakt., Parasitenk., II, 16, 681 and 769 (1906).

[2] This Journal, 28, 1437, (1906).

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digesting the unground sample with boiling water for three or four minutes, pouring off the water and repeating the operation. In the extract thus obtained fluorides were precipitated in the usual manner. In the case of barley, where reducing sugars were practically absent, the extraction was made on the ground sample but the digestion was carried out for half an hour at 40°-50°, a temperature below the gelatinizing point of starch.

Results.—The results obtained with a number of commercial malt liquors and with the principal raw materials of brewing are shown in the following tables. The results are stated in milligrams of fluorine per liter, or per kilogram in the case of solids. For convenience, the table of amounts of fluorine corresponding to the different "etching temperatures" given in the earlier paper[1] is here stated again in this form.

The values taken are based in each case upon the use of 150 cc. of the sample. With solids, the values will depend upon the weight taken and can be found readily by a simple calculation. Differences due to variations in specific gravity are so slight as to be neglected.

The samples of beers and ales represented about 50 different brands. The samples of malt and barley included both Eastern and Western growths.

TABLE 1.

MILLIGRAMS OF FLUORINE PER LITER (OR PER KILO) CORRESPONDING TO THE "ETCHING TEMPERATURES" WHEN 150 CC. (150 GRAMS) ARE USED.

Temperature	
79°-82°	10 to 40
113°	1 to 10
136°	0.2 to 10
173°-178°	0.04 to 0.2
213°-218°	Less than 0.04

TABLE 2.

FLUORINE IN MALT LIQUORS AND BREWING MATERIALS. MILLIGRAMS PER LITER (PER KILO).

	Number of Samples	40	30	10	8	3	1.0	0.5	0.2	0.04	Less than 0.04
Barley	15				1	4		1			9
Malt	15		2		13						
Brewing Sugar	9					1					8
Domestic Ale and Beer	34			4			9		21		
Imported Ale and Beer	15	3		5			2		5		

A sample of beer was brewed in the laboratory from materials which had been previously examined and had been found, with the exception of the malt, to be free from fluorides. This was done to determine if, under

[1] Loc. cit.

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these conditions the fluoride content of the malt would be sufficient to account for the amount found in the finished product. This was found to be true, since the resulting product gave a test at 143°, corresponding to an amount of fluoride equal to that present in the equivalent amount of malt used.

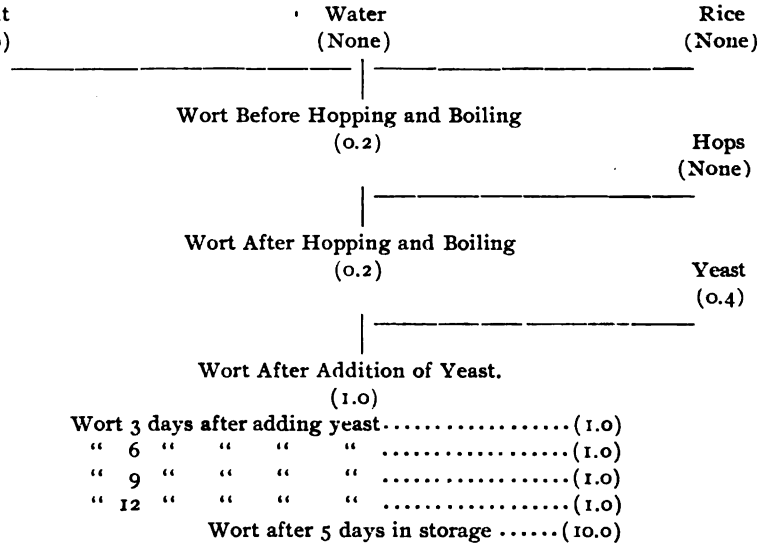
It was deemed advisable to follow, if possible, the brewing process as carried out on a commercial scale, noting the proportion of fluoride present at each stage of the brewing process.

Through the kindness of Dr. W. H. Walker it was possible to follow in this way one of the brews of a large brewing company, making examinations of the raw materials used, of the water, and of the wort at frequent intervals during the process of concentration and fermentation. The results are shown graphically in the accompanying tabular scheme.

They are calculated in each case to the amount of raw material that would be actually represented by 150 cc. of the finished product.

TABLE 3.

CHANGE IN FLUORIDE CONTENT DURING BREWING. MILLIGRAMS PER LITER (PER KILO).



In examining this table is should be borne in mind that the great difference shown in the beer before and after the period of five days storage is more apparent than actual. Owing to the limitations of the method it is impossible to follow closely gradual changes in the fluoride content until the amount present approaches one of the limits fixed by the etching temperature.

It is no doubt true that the content of fluoride was steadily increasing during the fermentation and that not until the final test was enough pre-

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sent to show at the 10 milligram point, although it had passed the 1 milligram point some time before.

It is also true that the presence of sugary matter prevents to some extent the precipitation of the fluoride, even when the latter is present. It is highly probable that the apparent increase in fluoride content is due rather to the decrease in sugar as the fermentation proceeded, and the consequent availability of the fluoride for precipitation.

Through the cooperation of a large malting establishment we were enabled to go one step further back and follow the malting process in its effect on the fluoride content of the grain. Samples were sent us of the barley, the water used for steeping, and dried samples of the malt at various stages from the steeping tank to the finished product. On these samples the following results were obtained:

	Milligrams per kilo
Hard steep water	10.0
Soft " "	None
Barley before steeping	3.0
Steeped barley	3.0
Malt 2 days old	3.0
" 4 " "	3.0
" as put on kiln	3.0
" from kiln	8.0

Summary.

From the results obtained two things are strikingly apparent. First, that the presence of a slight amount of fluoride in malt liquors is the rule rather than the exception, and second, that the principal source of this fluoride is the malt itself. In the majority of cases it is undoubtedly true that the proportion of fluoride in the beer is entirely accounted for by the malt.

This amount may be slightly increased in some cases by smaller quantities introduced through the use of brewing sugars, from the water, especially if artificially hardened by the use of gypsum containing fluoride, or from the yeast.

It is of course possible that fluorine was present in all the samples of barley and that the simple method used for the extraction failed to remove it, especially that present as insoluble calcium fluoride. A more probable explanation, however, is to be sought in natural geographical variations in the soil, the use of commercial fertilizers, such for instance as phosphate rock, notoriously rich in fluoride, and other primary agricultural factors. Judging from the results obtained on a considerable variety of samples, it would seem that one part of fluoride in 100,000 (10 mgs. per liter) was not too severe a standard to set for the maximum limit of permissible fluoride in malt liquors.

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The greater portion of the domestic samples examined did not contain over 1:5,000,000 (0.2 mg. per liter).

Testing a malt liquor by the method described, then, we should think that if 150 cc. contained enough fluoride to give a visible etching at 80°, the sample was open to suspicion as containing added fluoride.

In conclusion, the authors take pleasure in acknowledging their indebtedness to Miss Elizabeth Amison for much painstaking and careful analytical work.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
June, 1907.

FACTORS IN BORIC ACID MANUFACTURE.

BY JOHN WINKLER.
Received June 4, 1907.

One who may be interested in the subject of borax will find the phase relating to its occurrence, production and uses, in the U. S. Mineral Resources for any year from 1900 to 1905; the phase relating to its physiological action in Dr. H. W. Wiley's Report, Bull. 84 or Cir. 15; and the phase relating to its detection and estimation in minute quantity in foods in this Journal, July, 1906. For the analytical phase among the best references are: J. Soc. Chem. Ind., July, 1904; Sutton Vol. Analysis; Zeitsch anal. Chemie., **34**, (1900); Chemiker-Zeitung, Jan. 16, 1901. And for the geological phase the best works are those of Kemp, G. W. Miller, The Calif. State Mining Report 1892, The "Saline Deposits of California" by G. E. Bailey (Cal. State Mining Bureau S. F.).

These authorities seem to agree with the practical men in the borax fields that the origin of the borates must have been emanations from volcanic vents and hot springs; and likely in the form of boric acid carried by the steam and other gases; and that subsequently such borates as colemanite (which is borate of lime with water of crystallization), and others must have crystallized from lakes and springs on evaporation, and, of course, were deposited as strata. As a rule these strata are found associated with secondary clays, which clays may also be impregnated with borate. Borate formation appears distinctive.

A number of analyses of these borate clays show them to have the following general composition:

SiO_2	45-55 per cent.	Na_2O and K_2O	½-2½ per cent.
Al_2O_3	5-15 " "	CO_2	½-3 " "
FeO and Fe_2O_3	4-12 " "	SO_3	½-5 " "
CaO	7-15 " "	B_2O_3	0-30 " "
MgO	1- 4 " "	Org. matter moisture, considerable.	

The borates are mixed with gypsum and carbonates, which makes manufacture much more expensive. The sodium carbonate is mixed

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with sodium sulphate and other soluble salts. And that is the case in general.

The affinity holding boric acid to lime at ordinary temperatures appears to be not very great: Acid fumes in moist conditions like sulphur dioxide or nitric fumes, or even dilute acetic acid, decompose calcium borate readily and completely. Also, in Death Valley, and in other places, where sodium carbonate comes in contact with calcium borate, in warm moist condition, in contact with air, the sodium gradually displaces a part of the calcium, forming calcium-sodium borate, known as "cotton-ball," or ulexite. This is always found near the surface. Boiling with sodium carbonate readily transposes it further to borax. This was the way the first borax in Death Valley was made. In some marshes crude borax is actually disseminated through the clays.

The higher grade of calcium borate, say that running 30 per cent. or more in terms of boric acid or 45 per cent. in terms of crystallized borax, is shipped directly from the mine to the factory. A somewhat lower grade is first roasted at a red heat, when the borate loses its water and falls to a powder, and is then separated from the heavier gang, and shipped. At the factory the raw material is ground to a very fine flour and boiled for hours in iron drums with soda ash and bicarbonate of soda. The borax is then crystallized away from the sodium sulphate, which is generally present, (originally as gypsum in the ore), on iron rods. It is refined by recrystallizations. The bulk of it goes in the enamelling works: *e. g.*, a bath-tub is a cast iron trough coated with a borax enamel. (For description of this process see Trans. Am. Ceram. Soc., 8, 172-80, Ohio). The formulas of the mixtures are worked out by experiment and kept secret.

Some of the low grade ore (which by the way is of too low grade to boil directly with soda—profitably—too much bulk) is ground in water to a slurry, and decomposed by dilute sulphuric acid, or by sulphur dioxide fumes forced into it till all the boric acid is set free. In either case it is then diluted with water, agitated and allowed to settle; the cleared leachings evaporated by sun and wind in large solar vats; and during the process of evaporation, the acid is crystallized away as much as possible from the impurities, which are chiefly silicic acid and soluble sulphates.

According to Patent literature the Germans employ carbon dioxide under pressure instead of sulphur dioxide. The carbon dioxide is forced into the slurry till it becomes saturated with acid carbonate of calcium. Then the pressure is released. The calcium carbonate to a large extent precipitates. More CO_2 is then forced in; and process repeated till all of the borate is decomposed or nearly so. Now the calcium carbonate formed does not so readily counter-react with the freed boric acid in the cold, and especially where the slurry is saturated with carbon dioxide.

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There are some especial advantages to this procedure:

(1) The reagent, (which is one of the heavy items of expense) does not waste itself on the carbonates, which are generally present and sometimes to a considerable percentage.

(2) It does not introduce so many impurities into the liquors.

(3) Carbon dioxide can probably be generated more cheaply than other acid reagents:—*e. g.*, from coal. In burning coal the heat can be utilized for heating large quantities of water, which seems impracticable, so far, in sulphur furnaces.

In this country Blumenberg has devised and covered by patent a muffle in which sulphur dioxide is blown from burning sulphur (or pyrites) into the slurry until all the boric acid is freed. This does not require the high pressure of the carbon dioxide process; and, as against the sulphuric acid process, it attacks the impurities in the ore to a lesser extent. These impurities are silicates, the lower oxides of iron, aluminum and other bases. On the other hand, more or less, of the gas is carried out with the leachings, and oxidizes, in part, to sulphuric acid. However, the liquors are clear then, but become somewhat harder to evaporate upon concentration; and the loss of boric acid by volatilization becomes a trifle greater than in neutral solution. Nitric acid is not required; nor a sulphuric acid plant; but the boric acid plant has to be larger, since it takes much longer to decompose the slurry with the gas. The gas has to be blown in by an air compressor or other machinery, which may become expensive if not well regulated. This is not necessary in a sulphuric acid plant. The loss in gas is about the same in the slurry as in the acid chamber. Acid sulphites are not formed till after all the borate is decomposed. The sulphites of calcium and of other metals dissolve in the solution of sulphur dioxide. The calcium precipitates, (partly as sulphate) as soon as the gas oxidizes, or is whipped out by the wind.

Sulphur burning under forced draught, however, requires a special set of conditions, or a part of the sulphur will sublime; a large excess of air seems necessary both for oxidation and the cooling of the furnaces. For that reason the side-doors to the draw-furnaces have improved matters materially.

In the matter of leaching the old process has been to dilute the decomposed slurry with more water and agitate thoroughly, let settle, and allow the clear leachings to reconcentrate and evaporate in the sun and winds. This system is now to be superseded by a scheme of concentrating the pulp or slurry; then filter-pressing it, and crystallizing the acid from the concentrated solution. The cake, wherever possible, is to be manufactured into brick. This takes the industry away from the climatic elements and yields quicker returns. It is analogous to the case in

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cyaniding, where the slurry from the mills was run out of doors, and aerated for months to fully oxidize the ore, before it could be cyanided to advantage, but it is now roasted and cyanided at once.

Analytical Methods.

Qualitative:—A little of the finely powdered material in a butter dish is treated with enough of concentrated sulphuric acid to make a paste. Then a little wood alcohol is added. On igniting and stirring with a lead rod, a green flame indicates borate. The test is quite delicate. Wood alcohol gives a better test than grain alcohol.

For slurry, to determine undecomposed ore: A perforated 4-inch pipe-plug is screwed into a 4-inch coupling; a piece of canvas is laid in this cap and a little of the slurry is poured in. The cap is then screwed onto a 4 x ½-inch bushing, which bushing is in turn screwed onto a ½-inch steam line with a valve to regulate the steam. Steam is turned on a few minutes, which carries all of the free boric acid with it through the perforations, leaving the undecomposed borate behind. The above flame test is then applied.

Quantitative; Method I:—This is limited to ores or residues where concentrated sulphuric acid does not liberate acid fumes, except carbonate; that is to say, chlorides, nitrates, sulphites and similar salts must be absent. The method may, however, be altered so as to include at least a part of these, Put 1 g. of the finely flowered material into a 125 cc. flask; (0.5 g. if over 40 per cent. H_3SO_3). Mix thoroughly with about 1.5 cc. of sulphuric acid, sp. gr. 1.84; heat to 70°-80° to expel most of the carbon dioxide; let cool; connect to a condenser, and distill the boric acid over on steam-jet or steam-bath (not flame) with 6-10 cc. portions of wood alcohol, taking care that each portion is well over before adding the next. The alcohol is admitted to the flask through a stopcock. In the receiver should be such a volume of glycerol as to equal ⅛ the volume after titration. The glycerol should contain a little water, say 5-8 per cent. When the six portions are well over, the residue (should be small) must be tested by the flame test. If any "green" appears the assay must be repeated, using 7-10 cc. portions of alcohol; or a less quantity of ore. When the distillation is completed, add about 1 cc. o ½ per cent phenolphthalein to the receiver and mix well; and titrate with about N/5 sodium hyroxide free from carbonate. To standardize the alkali use from 0.2 to 0.4 g. of perfectly c.p. boric acid in place of the ore, and distill in exactly the same way. Then run "a blank," using only the 1½ cc. of sulphuric acid and subtract the amount of alkali required from the other readings. This gives good results. An improvement is to use a very concentrated aqueous solution of known strength of pure mannitol in place of the glycerol. A much sharper end point is then obtained. A volume of mannitol containing about 1 g. of mannitol will

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be found sufficient. Again, if hydrochloric acid or any other acid distils over, then in place of the glycerol or mannitol solution, put about an equal volume of distilled water into the receiver; and distil the boric acid over into this as before. When completed make neutral with sodium hydroxide free from the carbonate, using about one drop of *p*-nitrophenol (1 g. of *p*-nitrophenol dissolved in 75 cc. ethyl alcohol and 25 cc. of water added). Now add the same amount of mannitol in powdered form, and let dissolve. Titrate as before. The receiver should be a flask and kept cool during the distillation.

II. General Method:—When method I fails, the ore is decomposed as before with a very small excess of concentrated sulphuric acid, in a graduated flask, of about 80 or 100 cc. capacity. About 20 cc. of water are added; and, if necessary, a crystal or so of potassium chlorate, and the solution brought to a boil to oxidize the iron. When oxidized a slight excess of sodium carbonate is added and the solution is brought to a boil again. It is then cooled and diluted to the mark; an exact aliquot part of the clear liquor is taken (not over 25 cc.) and made just acid with drops of concentrated sulphuric acid, to one drop of very dilute methyl orange. It is then brought to a boil for a quarter of a minute (not longer); cooled, neutralized exactly by sodium hydroxide free from carbonate, adding (if necessary) another drop of the dilute methyl orange. About 1 g. of powdered mannitol is then added and dissolved; and the solution titrated with about N/5 sodium hydroxide and phenolphthalein. ($\frac{1}{4}$ cc.). If mannitol is not at hand, use neutral glycerol. (A volume equal to $\frac{1}{3}$ vol. after titration, deducting the amount required to bring the color.) If glycerol is not at hand, a little sugar may be boiled a few minutes in a little dilute sulphuric acid, making a very concentrated solution of sugar, and neutralized to phenolphthalein by sodium hydroxide free from carbonate. This mixture may be used instead of glycerol, but the end point is not very distinct. The fructose appears to be the active ingredient in this case.

When aluminum or chromium salts are present, instead of using sodium carbonate as the precipitant, nearly neutralize with sodium carbonate and boil with a slight excess of c.p. solid barium carbonate, making sure that the potassium chlorate has previously oxidized the iron.

The N/5 sodium hydroxide is standardized with c.p. boric acid in exactly parallel conditions.

III. The Iodate Method by Jones[1] is very highly recommended wherever there are no interfering ingredients, as iron, aluminum or chromium.

[1] Am. J. Sci., 1898, 147-153, or Sutton's Volumetric Analysis.

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IV. Mill Liquors:—By way of general precaution, boiling of liquors concentrates them and silicic acid, the heavy metals, ammonium salts, organic material, carbon dioxide and other gases must first be removed, if present. Boric acid is volatile, especially in presence of mineral acids; hence boric acid concentrates cannot be dried over steam, but only in a desiccator.

In evaporating boric acid solution to dryness in order to char organic material, etc., do not use sodium carbonate or bicarbonate (since that forms a clinker) but use c.p. barium hydroxide in slight excess. Boric acid is readily soluble in warm wood alcohol, but the borates are insoluble: a means of separating boric acid from borax, etc. C.p. boric acid should always be tested for impurities before using for standardization, *viz.*, sulphates, carbonates, chlorides, etc., and purified by recrystallization from boiling water. Of the oxidizing agents, barium peroxide, potassium bichromate, nitric acid or ammonium nitrate will not answer. Potassium chlorate and a drop of concentrated sulphuric acid, if necessary, is the best oxidizing agent so far, although bromine may be used with slightly higher results; but bromine in a hot climate fumes too much.

Take about 80 cc. of the mill liquor or solution in a flask; add a drop of concentrated sulphuric acid, if necessary, and a crystal or so of potassium chlorate, and just bring to a boil; let stand a few minutes. When oxidized or nearly so, add a slight excess of anhydrous pure sodium carbonate and bring just to a boil again. Draw off 25 cc. (not more) of the supernatant liquor, make slightly acid with drops of concentrated sulphuric acid, boil for a quarter of a minute, but not longer (this removes about all of the carbon dioxide) and titrate as in the previous methods.

If organic acids are present, the solution must first be made alkaline with barium hydroxide and evaporated to dryness in a small evaporating dish, and the residue very carefully charred with as low as possible heating. The solution is then redissolved with a little sulphuric acid and made up to the former volume. Also the other precautions relating to aluminum, chromium, etc., must be followed as in the previous methods. Further, if much potassium chlorate has to be used, an expansion factor must be determined, and the final result multiplied thereby.

In analyzing borate mixtures for other elements, a good way to begin is to set free the boric acid with a little concentrated hydrochloric acid in an evaporating dish, and on the steam bath, evaporate the boric acid away with pure wood alcohol (which leaves no residue of its own), until the flame burns perfectly blue. A little ferric chloride may thus be lost, but this can be avoided by using concentrated *sulphuric* acid instead of hydrochloric.

DAGGETT, CALIFORNIA, May, 1907.

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NOTES.

The Qualitative Detection of Sulphur Dioxide in Linseed Oil, Etc.—A rapid and sensitive method for detecting sulphur dioxide in various oils, by means of starch iodate paper, has been used by the writer, with success for a period of several years. Starch iodate paper is made by immersing filter paper in the following solution, and drying slowly.

100 cc. of boiling distilled water, is added to two grams of starch, care being taken to prevent lumps, then 0.2 gram of potassium iodate, which has been dissolved in 5 cc. of cold distilled water is added to the starch solution.

On testing a suspected sample of linseed oil, or other oils, which are of a high boiling point, the following is the most satisfactory method of procedure.

10 cc. of the oil is put into a test tube, about 150 × 18 mm. and a strip of the iodate paper, which has been slightly moistened half its length, is suspended in the mouth of the test tube. The oil is gradually heated until near the boiling point, when, if sulphur dioxide is present, it will appear instantly, by the characteristic blue reaction, at the junction where the paper has been moistened.

In the case of low boiling oils, such as washed petroleum, and coal tar oils, etc., it is most suitable to distill 100 cc. in a glass distilling bulb, using a short Liebig condenser, and placing the moistened starch iodate paper at the end of the condensing tube. The distillation should not be carried on too rapidly.

In conclusion, the writer would state that very good results were obtained in determining the presence of very slight traces of sulphur dioxide, which could not be practically determined by any other method.

2821 Reynolds St., Philadelphia. HENRY C. FREY.

Report of the Committee on Standard Methods for the Analysis of Iron.[1]—At the annual convention of the Association in 1905, this committee reported a method for the determination of silicon in iron, and last year added methods for determining total carbon and sulphur. The committee now adds methods for determining graphitic carbon, manganese and phosphorus, thus including all the determinations usually made on iron in which occasion for difference between the buyer and seller is apt to arise. This report will therefore include all the methods decided upon.

We would also like to call attention to the following quotation from the report of 1905, which indicates the intentions of these methods.

"In recommending the above method, it was recognized that it is almost an impossibility to get chemists to use a standard method in their daily work. Hence the above method, as recommended, is intended primarily as a check method in case of dispute between laboratories, or as between buyer and seller.

[1] From Transactions of the American Foundrymen's Association, Philadelphia Convention May 20-24, 1907.

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"Hence a method accurate in every point was sought, shortness being sacrificed to some extent to insure accuracy or against the chance of error by a careless operator. Little in the above is left to the judgment of the chemist.

"It will be further recognized that in the purchase and sale of pig iron or castings under specification, that standard methods are essential in in order to allow the parties of both parts to make their determinations with the assurance that, on the score of method, they are on the same footing."

We wish also to emphasize the ideas involved in the selection of members of this committee—that is to have representatives from commercial laboratories as well as works chemists, and to have members from different sections of the country. The success in carrying out these ideas will be seen by the following list of members:

Andrew A. Blair, Booth, Garrett & Blair, Philadelphia.

H. E. Diller, chemist, Western Electric Co., Chicago.

H. E. Field, metallurgical engineer, Mackintosh, Hemphill & Co., Pittsburg.

R. F. Flinterman, chief chemist, McCormick division, International Harvester Co., Chicago.

Allan P. Ford, metallurgist, Eaton, Cole & Burnham Co., Bridgeport, Conn.

J. O. Handy, chief chemist, Pittsburg Testing Laboratory, Pittsburg.

J. R. Harris, chief chemist, Tennessee Coal, Iron & Railroad Co., Birmingham, Ala.

H. C. Loudenbeck, chief chemist, Westinghouse Air Brake Co., Pittsburg.

R. S. MacPherran, chief chemist, Allis-Chalmers Co., Milwaukee.

W. G. Scott, chief chemist, J. I. Case Threshing Machine Co., Racine, Wis.

Henry Souther, Henry Souther Engineering Co., Hartford, Conn.

Prof. Thomas B. Stillman, Stevens Institute of Technology, Hoboken, N. J.

Determination of Silicon.—"Weigh one gram of sample, add 30 cc. nitric acid (1.13 sp. gr.); then 5 cc. sulphuric acid (conc.). Evaporate on hot plate until all fumes are driven off. Take up in water and boil until all ferrous sulphate is dissolved. Filter on an ashless filter, with or without suction pump, using a cone. Wash once with hot water, once with hydrochloric acid, and three or four times with hot water. Ignite, weigh, and evaporate with a few drops of sulphuric acid and 4 or 5 cc. of hydrofluoric acid. Ignite slowly and weigh. Multiply the difference in weight by 0.4702, which equals the per cent. of silicon."

Determination of Sulphur.—Dissolve slowly a three gram sample of drillings in concentrated nitric acid in a platinum dish covered with an inverted watch glass. After the iron is completely dissolved, add two grams of potassium nitrate, evaporate to dryness and ignite over an alcohol lamp at red heat. Add 50 cc. of a one per cent. solution of sodium carbonate, boil for a few minutes, filter, using a little paper pulp in the filter if desired, and wash with a hot one per cent. sodium carbonate solution. Acidify the filtrate with hydrochloric acid, evaporate to dryness, take up with 50 cc. of water and two cc. of concentrated hydrochloric

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acid, filter, wash and after diluting the filtrate to about 100 cc. boil and precipitate with barium chloride. Filter, wash well with hot water, ignite and weigh as barium sulphate, which contains 13,733 per cent. of sulphur.

Determination of Phosphorus.—Dissolve two grams samples in 50 cc. nitric acid (sp. gr. 1.13), add 10 cc. hydrochloric acid and evaporate to dryness. In case the sample contains a fairly high percentage of phosphorus it is better to use half the above quantities. Bake until free from acid, redissolving in 25 to 30 cc. of concentrated hydrochloric acid, dilute to about 60 cc., filter and wash. Evaporate to about 25 cc., add 20 cc. concentrated nitric acid, evaporate until a film begins to form, add 30 cc. of nitric acid (sp. gr. 1.20) and again evaporate until a film begins to form. Dilute to about 150 cc. with hot water and allow it to cool. When the solution is between 70° and 80° C. add 50 cc. of molybdate solution. Agitate the solution a few minutes, then filter on a tared Gooch crucible having a paper disc at the bottom. Wash three times with a three per cent. nitric acid solution and twice with alcohol. Dry at 100°-105° to constant weight. The weight multiplied by 0.0163 equals the per cent. of phosphorus in a one gram sample.

To make the molybdate solution add 100 grams molybdic acid to 250 cc. water, and to this add 150 cc. ammonia, then stir until all is dissolved and add 65 cc. nitric acid (1.42 sp. gr.). Make another solution by adding 400 cc. concentrated nitric acid to 1100 cc. water, and when the solutions are cool, pour the first slowly into the second with constant stirring and add a couple of drops of ammonium phosphate.

Determination of Manganese.—Dissolve one and one-tenth grams of drillings in 25 cc. nitric acid (1.13 sp. gr.) filter into an Erlenmeyer flask and wash with 30 cc. of the same acid. Then cool and add about one-half gram of sodium bismuthate until a permanent pink color forms. Heat until the color has disappeared, with or without the precipitation of manganese dioxide, and then add either sulphurous acid or a solution of ferrous sulphate until the solution is clear. Heat until all nitrous oxide fumes have been driven off, cool to about 15°; add an excess of sodium bismuthate—about one gram—and agitate for two or three minutes. Add 50 cc. water containing 30 cc. nitric acid to the liter, filter on an asbestos filter into an Erlenmeyer flask, and wash with 50 to 100 cc. of the nitric acid solution. Run in an excess of ferrous sulphate and titrate back with potassium permanganate solution of equal strength. Each cc. of N/10 ferrous sulphate used is equal to 0.10 per cent. of manganese.

Determination of Total Carbon.—This determination requires considerable apparatus; so in view of putting as many obstacles out of the way of its general adoption in cases of dispute your committee has left optional several points which were felt to bring no chance of error into the method.

The train shall consist of a pre-heating furnace, containing copper oxide (Option No. 1) followed by caustic potash (1.20 sp. gr.), then calcium chloride, following which shall be the combustion furnace in which either a porcelain or platinum tube may be used (Option No. 2). The tube shall contain four or five inches of copper oxide between plugs of platinum gauze, the plug to the rear of the tube to be at about the point where the tube extends from the furnace. A roll of silver foil

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about two inches long shall be placed in the tube after the last plug of platinum gauze. The train after the combustion tube shall be anhydrous cupric sulphate, anhydrous cuprous chloride, calcium chloride and the absorption bulb of potassium hydroxide (sp. gr. 1.27) with prolong filled with calcium chloride. A calcium chloride tube attached to the aspirator bottle shall be connected to the prolong.

In this method a single potash bulb shall be used. A second bulb as sometimes used for a counterpoise being more liable to introduce error than to correct error in weight of the bulb in use, due to change of temperature or moisture in the atmosphere.

The operation shall be as follows: To one dram of well mixed drillings add 100 cc. of potassium chloride solution and 7.5 cc. of hydrochloric acid (conc.). As soon as dissolved as shown by the disappearance of all copper, filter on previously washed and ignited asbestos. Wash thoroughly the beaker in which the solution was made with 20 cc. of dilute hydrochloric acid (1 to 1) pour this on the filter and wash the carbon out of the beaker by means of a wash bottle containing dilute hydrochloric acid (1 to 1) and then wash with warm water until all the acid is washed out of the filter. Dry the carbon at a temperature between 95° and 100°.

Before using the apparatus a blank shall be run and if the bulb does not gain in weight more than 0.5 milligram, put the dried filter into the ignition tube and heat the preheating furnace and the part of the combustion furnace containing the copper oxide. After this is heated start the aspiration of oxygen or air at the rate of three bubbles per second, to show in the potash bulb. Continue slowly heating the combustion tube by turning on two burners at a time, and continue the combustion for 30 minutes, if air is used; 20 minutes, if oxygen is used. (The Shimer crucible is to be heated with a blast lamp for the same length of time).

When the ignition is finished, turn off the gas supply gradually so as to allow the combustion tube to cool off slowly and then shut off the oxygen supply and aspirate with air for ten minutes. Detach the potash bulb and prolong, close the ends with rubber caps and allow it to stand for five minutes, then weigh. The increase in weight multiplied by 0.27273 equals the percentage of carbon.

The potassium copper chloride shall be made by dissolving one pound of the salt in one liter of water and filtering through an asbestos filter.

Option No. 1.—While a pre-heater is greatly to be desired, as only a small percentage of laboratories at present use them it was decided not to make the use of one essential to this method; subtraction of the weight of the blank to a great extent eliminating any error which might arise from not using a pre-heater.

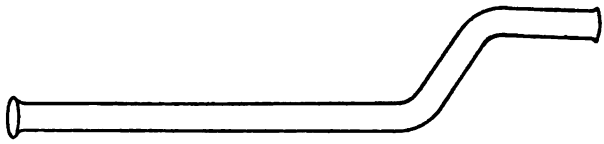
Option No. 2.—The Shimer and similar crucibles are largely used as combustion furnaces and for this reason it was decided to make optional the use of either the tube furnace or one of the standard crucibles. In case the crucible is used it shall be followed by a copper tube 3-16 inch inside diameter and ten inches long, with its ends cooled by water jackets. In the center of the tube shall be placed a disk of platinum gauze, and for three or four inches in the side towards the crucible shall be silver foil and for the same distance on the other side shall be copper oxide. The ends shall be plugged with glass wool, and the tube heated with a fish tail burner before the aspiration of air is started.

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Graphite.—Dissolve one gram sample in 35 cc. nitric acid (1.13 sp. gr.) filter on asbestos, wash with hot water, then potassium hydroxide (1.1 sp. gr.) and finally with hot water. The graphite is then ignited as specified in the determination of total carbon.

H. E. DILLER, Secretary.

Analysis of Fuming Sulphuric Acid.—The following method of analysis for fuming sulphuric acid has given excellent results for both speed and accuracy. Put about 15 cc. distilled water into a small Erlenmeyer flask, and then introduce a piece of 6 mm. glass tubing with a narrow constriction as shown in the cut. Allow a few drops of water to



trickle down the glass tube. Now weigh the sample in a Lunge pipette, and introduce the sample through the glass tube. The acid runs down through the tube and is absorbed by the water without spattering. Some fumes remain in the tube. By allowing a few drops of water to trickle down the tube, these fumes are completely absorbed. The analysis of one acid was checked within 0.05 per cent. ten times in succession by this method.

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NEW BOOKS

RADIOAKTIVE UMWANDLUNGEN. By E. RUTHERFORD. Translated by M. Levin. (Die Wissenschaft, No. 21). Braunschweig: F. Vieweg and Sohn. 1907. IX. 285 pp. Unbound, Mark 8.00; Bound, Mark 8.60.

The Silliman lectures, at Yale University, for the year 1905, were delivered by Prof. Rutherford. These lectures were published, in English, under the title, Radioactive Transformations (New York: Charles Scribner's Sons, 1906). The present work is a translation, into German, by Dr. Max Levin. It is less comprehensive than the author's book, Radioactivity, the second edition of which appeared in 1905. The new work deals especially with the marvelous spontaneous transformations which are taking place continuously in radioactive matter.

After an historical introduction, in which a general resumé of the development of radioactivity is given, the transformations of the element thorium are discussed. With clear and convincing argument, the author presents the facts which lead to the conclusion that thorium is very slowly decomposing. The first product of the decomposition is radiothorium; this, in turn, yields another radioactive product, thorium X., etc. The successive changes which have so far been established are as follows: Thorium→Radiothorium→Th X→Th Emanation→Th A→

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Th B→Th C. Each product has its own rate of change, which is independent of physical and chemical conditions. Radioactive phenomena are explained in terms of the Disintegration Hypothesis, proposed by Rutherford and Soddy. According to this hypothesis, an atom of any sort is a complex system; some atomic systems, those of radioactive elements, are unstable, with the result that a certain proportion of the elements break up or disintegrate per second; accompanied by the expulsion with enormous velocity, of α or β particles or both. The properties of the α particles led Rutherford to suggest that they might be atoms of helium; the experimental confirmation of this prediction by the observation, by Ramsay and Soddy, of the production of helium by the transformation of radium emanation has, more recently, been greatly strengthened by Debierne's demonstration of the production of helium by actinium.

It is shown in the following chapters that the changes in radium, actinium and uranium are to be explained by analogous series of transformations. The slowly changing products of radium are especially interesting; these are almost certainly the active constituents of radiolead, radiotellurium and polonium. In the chapter devoted to the origin and life of radium, it is shown that this element is, without doubt, a transformation product of the element uranium.

The subject matter of the book is well chosen and admirably presented and constitutes one of the most interesting topics in physical science. Coming as it does from a leader in this special field of investigation, the book is authoritative and will naturally take a permanent place in the literature of the subject. Dr. Levin's translation, which follows the original closely, is supplemented by occasional footnotes on the newer developments of the subject. HERBERT N. MCCOY.

THE BACTERIOLOGICAL EXAMINATION OF WATER SUPPLIES. By WILLIAM G. SAVAGE, B. Sc., M. D. (Lond.), D. P. H. and Professor of Pathology, in charge of the Bacteriological Department, University College, London. P. Blakiston's Son & Co., Phila., 1906. Price, $2.50 net.

Water bacteriology, one time an obscure branch of medical bacteriology, later treated more fully in general works on water analysis and water supply engineering, has in the past few years established its just claim to recognition as an independent branch of applied science. This is well illustrated by the appearance of the present work, the third of its kind, devoted wholly to this special branch of bacteriology. The author states in his preface: "Unfortunately, many of the data upon which the bacteriological examination of water is based have not passed beyond the region of controversy, and on not a few questions—some of which are of much importance—each bacteriologist is, at present, a law unto himself." In such cases the endeavor is made to give the best available information and to draw definite conclusions therefrom. In this regard the author

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shows familiarity with the best work in this field and by his excellent treatment and logical deductions has done much to clear up the debated points referred to.

The first chapter deals with the influences affecting bacteria in water. The grouping of the bacteria found in waters into (1) normal inhabitants, (2) unobjectionable aliens, and (3) objectionable aliens, is a fortunate conception. The discussion of the effect of light, agitation, temperature, dilution, sedimentation, food supply and microbe products upon the self-purification of streams is thorough and the conclusions drawn are based upon a large amount of experimental work, citations of original sources being given freely. The predominating influence of sedimentation is properly emphasized. The statement (p. 3) that "sewage entering a river will charge the water with vast numbers of its own bacteria alien to a pure water, yet twenty or thirty miles lower down, if no fresh additions have been made between, the water will be free, or practically free, from organisms of sewage origin," is rather a sweeping conclusion upon a vital point in water bacteriology. Although apparently supported by excellent bacteriological investigations, there is strong epidemiological evidence on the other side and the whole matter is at present in an unsettled state. In any case it will be conceded that the *distance* from the point of infection is the least important factor, the *time* of flow and opportunity for *sedimentation* being the vital factors.

In Chapter II, the bacterial content of normal waters, and the subject of standard media are discussed. On p. 23 the table taken from a paper by Gage and Phelps is misinterpreted to show that on Nährstoff agar the number of organisms found in pure ground waters was as great as in sewage. The fault lies perhaps in the original table in which a percentage basis of statement is used. The actual numbers in the two waters are not comparable with each other.

The two chapters following are devoted to the bacteriology of excreta and of soil respectively and contain much valuable material.

Chapter VI takes up *B. coli* and allied forms, including organisms of the hog cholera group, *B. lactis aerogenes* and *B. cloacae*. The various sets of diagnostic characters which have from time to time been proposed for the identification of *B. coli*, including those recommended by the English and the American Standard Methods Committees, are fully discussed. From these the author selects what he considers essential and recommends the following tests as necessary and sufficient for the complete determination of that organism:

A short bacillus with rounded ends, no spores, motile.
Decolorized by Gram's method.
Characteristic growth on gelatin.
Acid production and coagulation in litmus-milk.
Production of indol.

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Production of a considerable quantity of acid in litmus-whey.
Production of acid and gas in glucose and lactose media.
No fermentation of starch or saccharose.
A positive neutral red reaction.

The perplexing question of atypical forms is dealt with and the position taken that these are less and less significant as they depart from the normal type, and in quantitive work should be so weighted in the final estimation of the water.

In the chapter on the Eberth group a most excellent summary of our knowledge of the typhoid and dysentery bacilli is given, special attention being devoted to the question of the viability of the typhoid organisms.

The chapter on "Other Intestinal Bacteria" takes up the streptococcus group, *B. enteritidis sporogenes* and the cholera and other vibrios in the same thorough manner.

A chapter on "The Content of Various Waters in Regard to the Presence of *B. coli*, *B. enteritidis sporogenes and streptococci*" is followed by two chapters on "Bacterial Indicators of Pollution" and one on "Interpretation of Results." To the reviewer's mind these chapters are the best part of the book and constitute the most satisfactory discussion of these perplexing questions extant, and will place water bacteriology upon a firmer scientific basis than it has heretofore enjoyed. The conclusions are so thoroughly reasoned out that any attempt to abstract them in a review would be futile. Great reliance is placed upon *B. coli* properly determined, and less upon streptococci and *B. sporogenes*.

Part II, about one-third of the book, is devoted to laboratory methods. It contains among other things a valuable chapter on the typhoid organisms, giving descriptions of the best methods which have been proposed for the detection of this bacillus.

An appendix gives in summary the procedure recommended for the bacteriological examination of a water, and methods of preparing the ordinary standard solutions and media. An extensive bibliography completes the work. It is apparently an oversight that, in the bibliography, which is quite rich in American citation, Prescott and Winslow's "Water Bacteriology" is not mentioned. EARLE B. PHELPS.

SOLUBILITIES OF INORGANIC AND ORGANIC SUBSTANCES. A Handbook of the most reliable quantitative solubility determinations. Recalculated and compiled by ATHERTON SEIDELL. 8 vo. X + 367 pages. D. Van Nostrand Company, New York, 1907. Price $3.00 net.

This handbook of solubilities should find a place in every laboratory and chemical library, for it contains in one volume the solubilities of both organic and inorganic substances, not alone in water, but also in the other common solvents, and, in many cases in salt or other solutions as well. In including organic substances it is a distinct improvement

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upon Comey's "Dictionary", which excluded the solubilities of metallic salts of even the common organic acids.

The author has not only collected his material from the original sources, but, after recalculating the various determinations to a common basis and plotting the curves of the results, has selected the most reliable values, when the data at hand are not too discordant. This feature, for the average chemist, is of particular importance, especially as from the complete references given the investigator may calculate, if he desires a value for himself, or compare the actual experimental results.

Naturally, as the author states, it is impossible to make such tables complete, for solubility determinations are often incidental to other investigations and thus are not included in the titles. What the author has done is to examine the indices and tables of contents of twenty-five of the chemical journals issued since 1875, and to consult all articles in these, as well as in other journals to which references were made. The tables are arranged alphabetically, but there is also an index with cross references, so that the subject matter, which is brought up to November, 1906, is instantly available. Certainly the chemical public owes a debt of gratitude to Dr. Seidell for his painstaking work.

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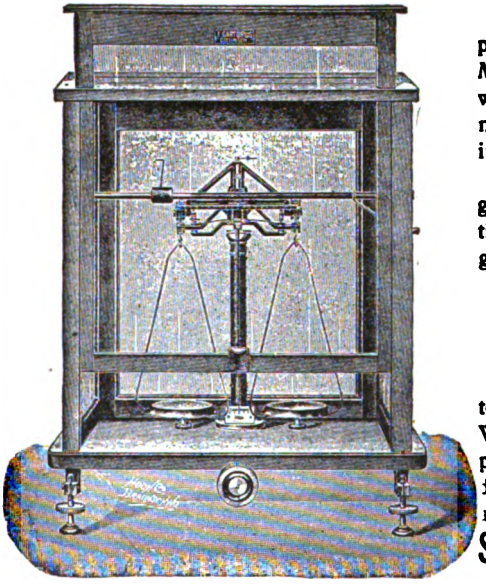
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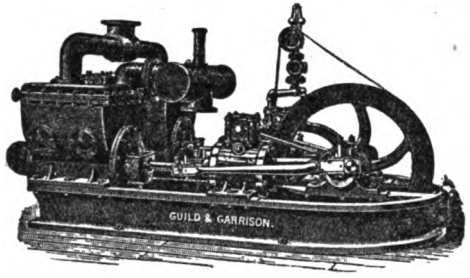
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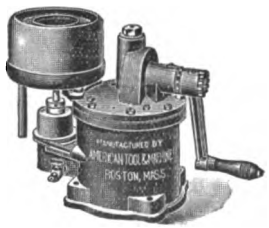
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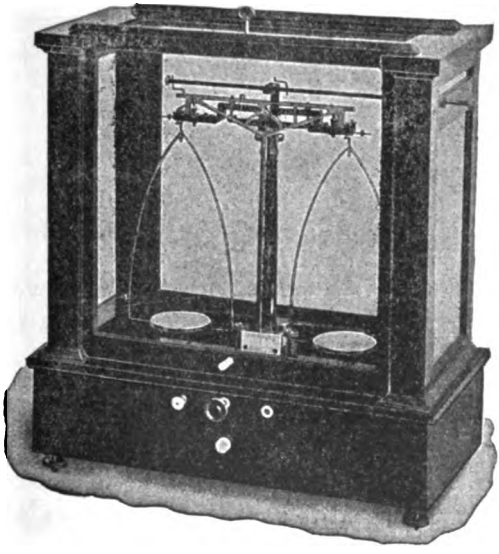
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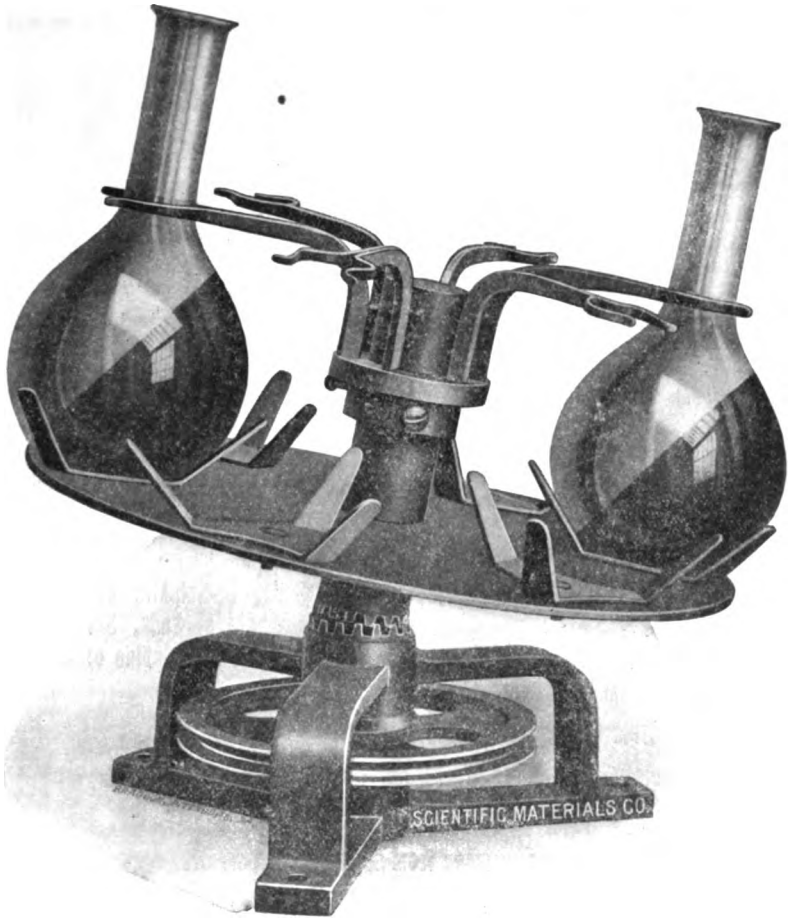
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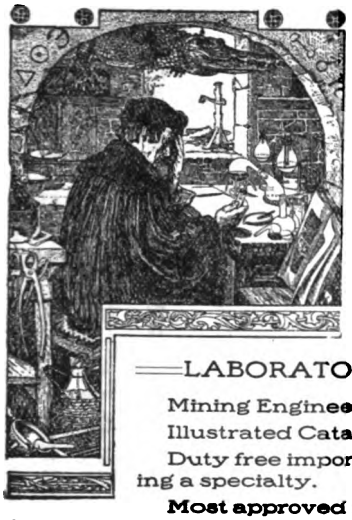
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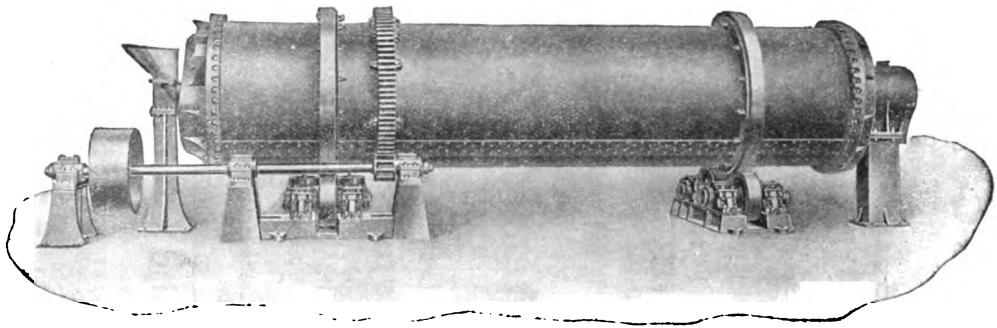
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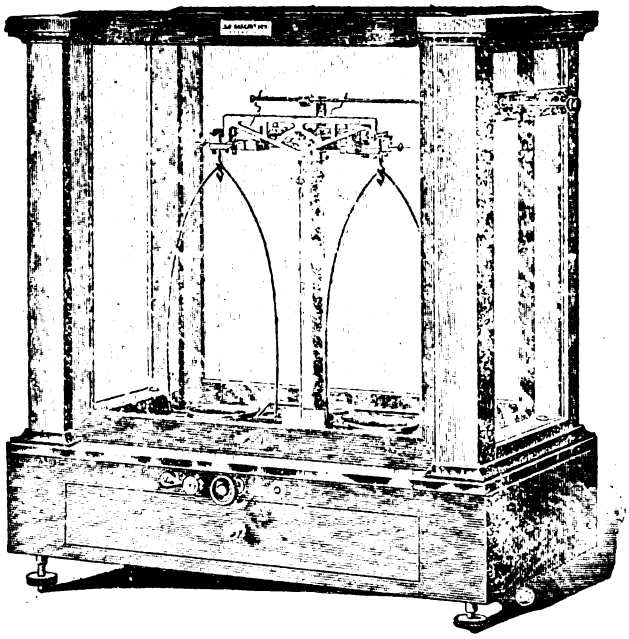
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CALORIMETRIC RESISTANCE THERMOMETERS AND THE TRANSITION TEMPERATURE OF SODIUM SULPHATE[1].

BY H. C. DICKINSON AND E. F. MUELLER.

Received August 11, 1907.

I. Calorimetric Resistance Thermometers.

Of the methods in use for temperature measurement the variation in resistance of metallic wires affords probably the most accurate means of obtaining differences of temperature over a limited range. When the resistance material is a pure metal, resistance is in most cases a simple function of temperature. The metal generally used has been platinum, on account of its high specific resistance, high melting point and freedom from oxidation.

Construction of the Thermometers.—A form of resistance thermometer for calorimetric work was constructed as follows: four leads of thin copper strip about 15 cm. long, 4 mm. wide, and 0.12 mm. thick, are each fused[2] to a piece of 0.1 mm. platinum wire about 10 mm. long. The leads are then laid side by side, separated by thin mica strips, and one pair is connected to the ends of a coil of about 10 cm. of 0.02 mm. platinum wire wound in a flat coil on the end of one of the mica strips; the other leads are connected by fusing together the ends of the short platinum

[1] Published in full in Bull. Bureau of Standards, 3, 1907.

[2] In making up these thermometers it was found impracticable to wind the coils after fusing to the leads, and to overcome the difficulty of fusing wires so fine as 0.02 mm. in somewhat inaccessible positions an arc was used. The arc was formed between a small graphite pencil and one of the terminals to be fused, when the other terminal was brought up and the two connected. After a little practice this could be done quickly and neatly. This same method has since been used to advantage in fusing together wires of different materials and sizes. The platinum terminals also were fused to the copper leads by the same method. The fusing of copper wires is more easily effected when borax is used as a flux. It is necessary to regulate both the voltage and the resistance in series with the arc for different sizes of wire.

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terminals. This second pair of leads is used to compensate for varying depth of immersion.

The leads and coil thus prepared were enclosed in a flat sheath of thin copper (0.12 mm. thick) and insulated from it by thin mica. The sheath was then soldered up along the side, copper-plated, and then gold-plated to protect it from oxidation. When finished it was about 7 mm. wide and 1 mm. thick, somewhat thinner at the coil. Finally it was sealed into a head of hard rubber, which serves to hold the flexible leads to the bridge, and covers containing a drying salt were also added.

This thermometer for calorimetric work has the following advantages: (a) very small time lag, (b) small water equivalent, (c) small thermoelectric effects due to the copper-platinum junctions, which are very close together, (d) high resistance (about 30 ohms in ice), (e) heat conduction by the leads affecting the temperature of the coil is not noticeable when the immersion is as much as 5 cm., (f) the resistance is made independent of depth of immersion by the use of compensating leads, (g) the insulation resistance has always been over 100 megohms.

Resistance Measurements.—Measurements of resistance were made by the Wheatstone bridge method using a bridge constructed especially for resistance thermometry. This bridge has an adjustable resistance of 110 ohms, the smallest coils being 0.01 ohm. In place of a bridge wire three shunt dials are used, giving steps of 0.001, 0.0001 and 0.00001 ohm respectively. The galvanometer used was of the Broca type and was so adjusted that a change of 0.0001 ohm, corresponding to 0.001° in temperature, gave a deflection of 1 mm. on the scale.

The bridge was calibrated several times during the progress of the work. All resistance measurements were made by reversing both battery and galvanometer connections to eliminate any small thermoelectric effects. A Griffiths thermoelectric key was used. The ratio arms were also reversed during each measurement.

Calibration of the Thermometers.—The formula proposed by Callendar $t - pt = \delta\left(\frac{t}{100} - 1\right)\frac{t}{100}$ where $pt = \frac{R_t - R_0}{R_{100} - R_0} \times 100$ was used as the basis of the calibration. The fundamental interval, R_{100}—R_0 was determined by measuring the resistance in ice and in steam in the usual manner. In Table I are given the values found at different times.

The constant δ was determined by comparing each resistance thermometer at 30°, 40°, 50°, 60°, 70°, with four primary standard mercurial thermometers of the Bureau of Standards. By an elaborate intercomparison the relation of each of these thermometers to the mean scale of the Bureau, which is defined by 16 thermometers calibrated at the International Bureau, and which have been shown to be in agreement with the Inter-

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TABLE I.

VALUES OF $R_{100} - R_0$.

Date	Thermometer A R_0	Thermometer A $R_{100}-R_0$	Thermometer B R_0	Thermometer B $R_{100}-R_0$
10- 6-06	29.00548	9.75060	28.94158	9.76746
		9.75068		9.76755
10- 8-06	29.00498	9.75079	29.94128	9.76777
		9.75097		9.76777
10-12-06	29.00530	9.75055	28.94160	9.76747
		9.75055		9.76709
10-18-06	29.00570	9.75063	28.94202	9.76720
		9.75062		9.76720
1-18-07	29.00579	9.75091	28.94230	9.76717
		9.75062		9.76728
		9.75019		
2-27-07	29.00603	9.75111[1]	28.94260	9.76791[1]
		9.75115[1]		9.76800[1]
7-11-07	29.00564	9.75062		
		9.75068		
7-12-07	29.00568	9.75065	28.94200	9.76727
		9.75033		9.76735
		9.75051		
	Mean	9.75062		9.76738
		± .00003		± .00003

national Hydrogen scale, had been established. Table II gives the results of this calibration, which shows that the platinum thermometers may be used to reproduce the International Hydrogen Scale to about 0°.002.

TABLE II.

VALUES OF δ.

Thermometer A					Thermometer B				
Point	$t-pt$	δ	Obs.-mean	Residual in temp. C	Point	$t-pt$	δ	Obs.-mean	Residual in temp. C
30°	0°.3264	1.560	+.006	0°.0013	30°	0°.3276	1.565	+.009	0°.0019
40°	0°.3711	1.548	—.006	0°.0014	40°	0°.3707	1.547	—.009	0°.0021
50°	0°.3890	1.556	+.002	0°.0005	50°	0°.3897	1.559	+.003	0°.0008
60°	0°.3722	1.550	—.004	0°.0010	60°	0°.3742	1.558	+.002	0°.0005
70°	0°.3269	1.554	.000	0°.0000	70°	0°.3259	1.550	—.006	0°.0013
	Mean	1.554	.004	0°.0008		Mean	1.556	.006	0°.0013

II. The Transition Temperature of Sodium Sulphate.

Since it has been shown that the relation between platinum temperature and the International Hydrogen Scale in the interval 0° to 100° may be given by a single constant (δ) it is evident that this constant might be equally well determined at a single temperature (in addition to the two fixed points) if the determination were made with sufficient accuracy. The work of Richards[2] and of Richards and Wells[3] has shown

[1] Not used in mean.

[2] Am. J. Sci., 6, 201, 1898.

[3] Pr. Am. Acad. Arts and Sci., 38, 431, 1902.

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that the transition point of sodium sulphate serves to fix a definite temperature which would be suitable for such determinations.

The care with which this work was done and the small probable error deduced from the observations require that anyone attempting to repeat the work should have exceptional facilities for obtaining accurate results. On the other hand, it is very desirable to secure a further check on a point so important, in view of its proposed use in the calibration of calorimetric thermometers.

It was decided to use the two platinum thermometers, calibrated as above described, in a redetermination of this temperature. While this is an indirect method, it has certain advantages over a direct determination with mercurial thermometers. In the first place, the platinum temperature could be determined to about 0°.001 by a single observation so that the errors in referring the point to the platinum scale become almost negligible and the whole problem is reduced to the relation between the platinum scale and the hydrogen scale, *i.e.*, the accuracy of mercurial thermometers.

Since the four thermometers used at each point have not only been calibrated at the International Bureau, but have been compared with a number of other primary standards also calibrated there and some of them directly compared with the standards of the International Bureau, they offer a means of reproducing the international hydrogen scale with the highest accuracy.

Moreover, the mercurial thermometers were used under conditions most favorable to attaining accurate results, *i.e.*, with total immersion, reading at principal calibration points where their indications are most reliable and reading with a rising meniscus. This avoids one of the largest sources of error in using mercurial thermometers, *i.e.*, the determination of a fixed point. In addition, as has been shown, the hydrogen scale represented by these platinum thermometers was obtained from the mean of observations taken at 30°, 40°, 50°, 60°, and 70°, so that in fact, the determination of the transition temperature 32°.38, rests upon observations of four thermometers at each of five points.

Method of Experiment.

The arrangement of the apparatus is shown in the accompanying figure, Fig. 1. (B) is a cylindrical brass case 6 cm. in diameter and 24 cm. long, which was immersed to the point (D) in a water bath ordinarily used for testing clinical thermometers. By this means the external temperature was regulated and could be maintained constant to 0°.1 for any length of time. The salt was contained in a strong test tube (N), 3 cm. in diameter and 15 cm. long, holding about 100 grams. Smaller tubes holding about 50 grams were also used in some of the preliminary work. The head of the thermometer (T) was held in place by a cork

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(C) fitted into a removable sleeve (S). The salt was thus entirely enclosed in an air space at the temperature of the surrounding water.

The first experiments were made on a sample of "Kahlbaum" sodium sulphate. Following the procedure of Richards, the crystals were first

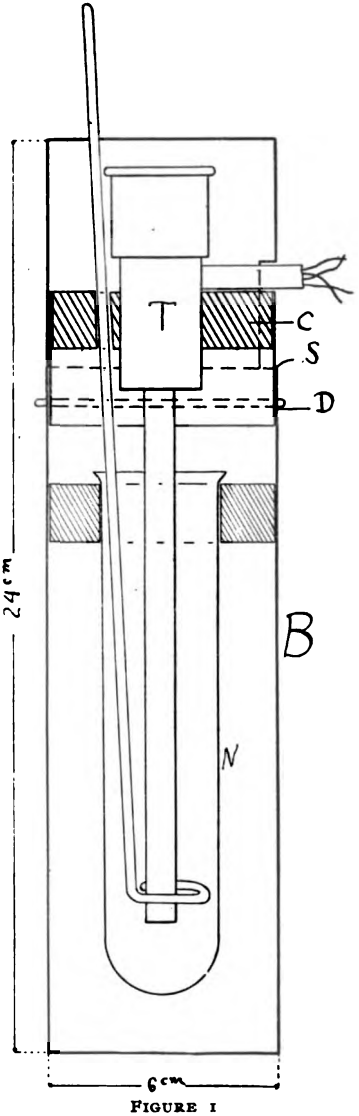


FIGURE 1

broken up rather fine in a mortar, then melted in the test tube by dipping in warm water until the mass could be readily stirred. The tube was then placed in position, the thermometer inserted, and readings taken at intervals during several hours. These observations showed that

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no very definite equilibrium had been established. Stirring the contents of the tube and small changes in the external temperature produced changes amounting to over 0°.01 even after two hours. The procedure was therefore slightly modified, as follows: As the crystals seemed rather moist, a small quantity of the anhydrous salt was first added and the crystals were almost entirely melted. Recrystallization was then started by running cold water over the tube. In this way a perfectly definite temperature was secured within five minutes after starting the experiment. It was found later that the addition of anhydrous salt was unnecessary, as enough was formed during the process of preparing and melting. The procedure just indicated was followed in all subsequent experiments.

The Effect of External Conditions.

In one experiment the external temperature was kept at 33° for an hour and the temperature of the salt was observed at intervals. These observations showed variations of about 0°.0005. The temperature was then dropped to 32° for an hour, but no larger variations were observed. When the temperature was dropped to 23° and maintained for about forty-five minutes, until the salt could no longer be stirred, no changes exceeding 0°.001 were observed in the transition temperature. On raising the external temperature to 43°, a rise of about 0°.003 was observed after thirty minutes, but it was noted that the salt was almost completely melted. The temperature was again lowered to 33° and the original value was found. The experiment of lowering the temperature was tried a number of times with the same result. Richards found that lowering the outside temperature two or three degrees lowers the temperature of the salt by about 0°.01. It seems probable that the procedure followed in the present instance, whereby new crystals are formed by sudden cooling, makes the transition temperature more definite and less dependent on external temperature. In this connection it should be pointed out that when the cooling was omitted the variations were not larger than the accidental errors of mercurial thermometers. These irregular observations, moreover, fell on both sides of the final value.

To test further the influence of external conditions a smaller test tube was used. The salt was first melted in a large tube and the temperature observed; some of it was then transferred to the smaller tube, where the same value was again found. This experiment further indicates that the effects of superheating, conduction down the thermometer stem, etc., were negligible. When the smaller tube was used, however, the external temperature had to be more carefully regulated, as a difference of 5 degrees from the transition point, if maintained for some time, began to affect the readings. Stirring the salt usually produced a small rise of less than 0°.001, which disappeared in two or three minutes.

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Impurities.

It seemed desirable to determine directly the error which might be introduced by the presence of impurities in the salt. Since the transition temperature must be determined with a mixture of crystals and solution, and the effect of the impurity, except in some special cases, varies with the relative amount of the two present, it is evident that this effect will not remain constant. The values quoted in the table below are therefore *only approximate*, but serve to show what effect and range of variation may be expected in the transition temperature.

TABLE III.

EFFECT OF IMPURITIES.

Impurity	Lowering of transition point for the following—					
	0.2 per cent. NaCl	0.08 per cent. NaCl	0.05 per cent. NaCl	0.01 per cent. NaCl	0.1 per cent. K_2SO_4	0.1 per cent. $(NH_4)_2SO_4$
	0°.1885	0°.0873	0°.0505	0°.0147	0°.0620	0°.0937
	0°.1942	0°.1019	0°.0486	0°.0147	0°.0607	0°.0922
	0°.1942	0°.1019	0°.0490?	0°.0147		0°.0911
Mean lowering	0°.193	0°.100	0°.049	0°.015	0°.061	0°.092

From the preliminary determinations it may be concluded that: (*a*) the transition temperature of sodium sulphate is definite to 0°.001; (*b*) within a considerable range the transition temperature is not affected by external conditions (temperature and pressure); (*c*) the presence of 0.001 per cent. of other salts may lower the transition temperature by 0°.001. From the latter consideration it appears that if samples made by different methods give different values the higher is to be chosen as representing the purer salt.

Final Determination.

For the final determination four samples prepared by the chemical division of the Bureau of Standards, were used. No. 1 was prepared from Kahlbaum's sodium sulphate three times recrystallized. No. 2 was the same salt five times recrystallized. No. 3 was prepared by neutralizing the carbonate and was four times recrystallized. No. 4, was the same, five times recrystallized. Table V shows values obtained for the different samples with the two thermometers.

TABLE IV.

Date	Therm. "Kahlbaum"	Temp.	Mean	Date	Therm.	Temp.	Mean
					No. I.		
1-4-07	A	32°.3812		1-12-07	A	32°.3832	
1-8-07	A	32°.3798			B	°.3841	32°.384
	B	°.3789			No. III.		
3-7-07	A	32°.3798		1-12-07	A	32°.3812	
	B	°.3773	32°.380		B	°.3818	32°.382
	No. II				No. IV.		
1-7-07	A	32°.3798		1-5-07	A	32°.3855	
	B	°.3796			B	°.3860	
1-8-07	A	32°.3819		1-8-07	A	32°.3855	
	B	°.3813			B	°.3834	
1-12-07	A	32°.3799		1-12-07	A	32°.3812	
	B	°.3806	32°.381		B	°.3818	32°.384
							32°.383

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The agreement of the two thermometers and the constancy of the values for each sample taken at different times show that the differences observed represent real differences in the transition temperature for the different samples. There is reason to believe that sample No. 2, which gives a low value, had been accidently contaminated with some of the solution used in cleaning the tubes. It may be noted that the constancy of the indications for the various samples with varying conditions is not necessarily a proof of their purity, since any impurities which were not removed by recrystallization would have an effect independent of the relative amount of crystals and solution present. Samples prepared from the carbonate are less likely to contain impurities of this kind. Since differences between different samples are probably due to impurities which lower the transition temperature, the higher values may be taken as more nearly representing pure salt. The mean value from samples Nos. 1, 3, and 4 is 32°.383. But, for the reasons given above, the higher values are entitled to greater weight so that the most probable value from these observations is 32°.384.

Conclusion.

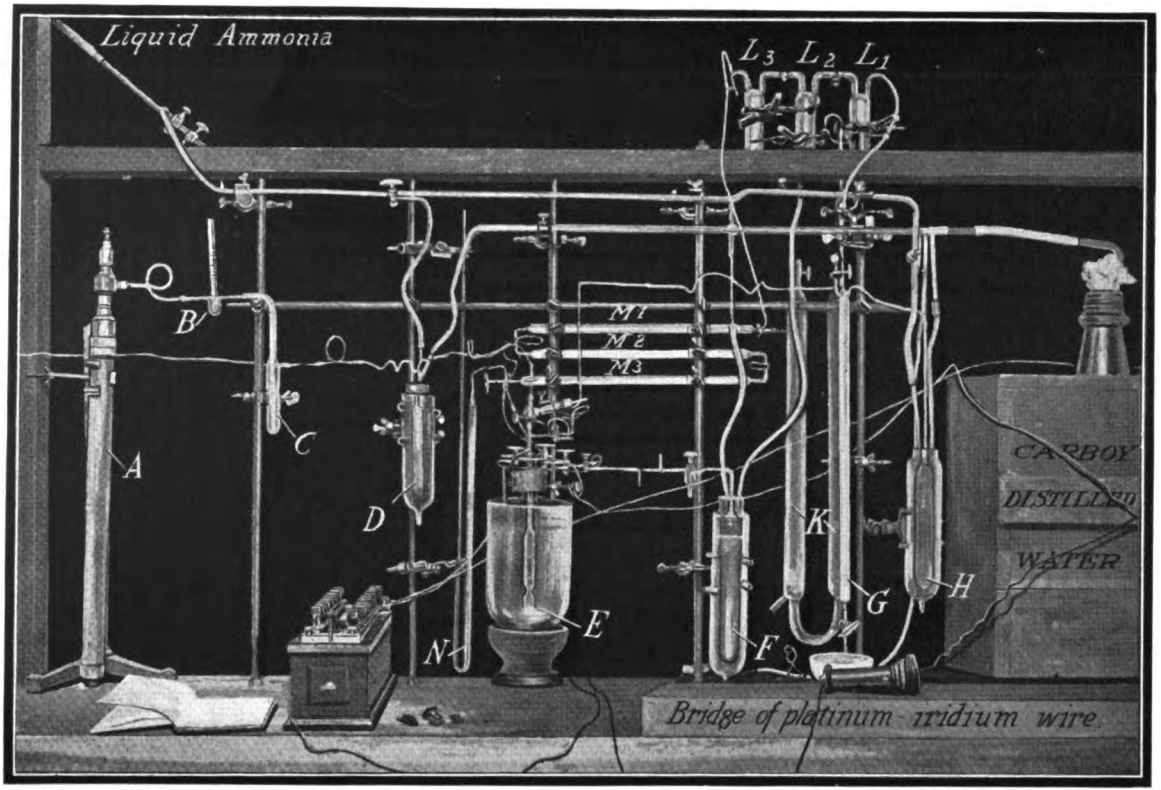
A special form of resistance thermometer, intended for calorimetric work, has been found applicable for general temperature measurement in the interval 0° to 100°. Two of these thermometers have been compared with eight primary standard mercurial thermometers, representing the mean temperature scale of the Bureau of Standards, at the temperatures 30°, 40°, 50°, 60°, and 70°. This calibration has shown that the Callendar formula $t-pt=\delta(\frac{t}{100}-1)\frac{t}{100}$ may be used to define the relation between the platinum scale of these resistance thermometers and the mean scale of the Bureau of Standards to within 0°.002. By using these calibrated thermometers the transition temperature of sodium sulphate has been determined and found to be 32°.384 for the purest salt. Resistance thermometers for use in the interval 0° to 100° may be calibrated to the highest degree of accuracy by using the Callendar formula and determining the constant δ from the transition temperature of pure sodium sulphate, 32°.384. These thermometers may be used to reproduce the international hydrogen scale of temperature to within 0°.002 or 0°.003.

In conclusion the authors wish to express their obligations to Dr. C. W. Waidner for many valuable suggestions throughout the course of the present investigation, to Dr. F. A. Wolff, who had charge of the calibration of the resistance bridge, and to Dr. Helen Isham, who prepared the samples of sodium sulphate used in determinations of the transition temperature.

BUREAU OF STANDARDS,
Washington, D. C.

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THE ELECTRICAL CONDUCTIVITY OF METHYLAMINE SOLUTIONS.

By E. C. Franklin and H. D. Gibbs.

Received July 12, 1907.

Since methylamine has been shown to possess a rather wide solvent power,[1] and to give solutions which in some cases are possessed of marked electrical conductivity,[2] it has been deemed worth while to extend the work of Gibbs on the properties of methylamine, to a quantitative study of the electrical conductivities of the solutions. The plan had been formulated of making measurements on a selected list of solutions, chosen to cover the field as well as possible, but as an unfortunate result of the earthquake of last April, the investigation was brought to a sudden close just as the work of making the measurements was well under way. It has been the expectation of the authors to take up again this investigation and finish a rather extended series of observations before publishing, but as a result of the junior author's transferring his field of activities to the Philippines, it has been determined to publish the data so far obtained.

Description of the Apparatus, Method of Manipulation.—The apparatus employed was, in principle, essentially the same as that used by Franklin and Kraus,[3] in their measurements of the conductivity of liquid ammonia solutions, with such modifications as the nature of the solvent seemed to require.

A is a steel cylinder containing the stock of methylamine. C is a filter tube which is introduced into the train for the purpose of removing any solid impurities which might be carried over with the gas.[4] B is a manometer used as an aid in regulating the flow of gas. D is a receiver into which the gas is condensed and retained until the pure liquid is required in the conductivity cell. E is the conductivity cell with its connections. E^1 is the constant temperature bath of ice and water. F is a receptacle for receiving the solution after removal from the conductivity cell. Before beginning a series of measurements this tube is evacuated through the stop-cock, S^{10}, and is kept cool by a bath of liquid ammonia. After a series of measurements is finished, F is removed and sealed before the blow pipe, thus permitting the operator to recover the expensive solvent. G is a pressure regulator devised for the purpose of regulating the boiling point of the solution in the conductivity cell, E, to the temperature of the bath, E'. The tube from the stop-cock, S^7, delivers the gas through pin hole openings under the mercury column, G, which latter may be adjusted to any desired height. The methylamine which escapes from the conductivity cell by way of this pressure

[1] Gibbs, This Journal, 28, 1395.

[2] Gibbs, loc. cit., and Franklin and Kraus, Am. Ch. J., 24, 90.

[3] Am. Ch. J., 23, 277.

[4] Vide Franklin and Kraus, Am. Ch. J., 23, 278.

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regulator is condensed in the cell H, which at the end of a series of measurements is removed and sealed, thus effecting a saving of the methylamine. Liquid ammonia for condensing the methylamine in the receptacles D, F and H, is delivered from a cylinder of the commercial liquid through the tube I. Ammonia gas is carried to a carboy of water through the tube I'. Pure, dry hydrogen for stirring the solution and removing it from the conductivity cell is delivered to the apparatus under pressure at the stopcocks S^6 and S^9. It is to be noted that the methylamine after leaving the steel cylinder and the short piece of lead tubing leading from it, comes in contact only with the glass of the apparatus, the platinum electrodes of the conductivity cell, and the hydrogen used for stirring the solution, for the various glass portions of the apparatus are sealed together by means of flexible joints made by drawing the tubing to capillaries. The hydrogen which comes in contact with the solutions is produced by the electrolytic decomposition of dilute sulphuric acid in the tube, K, (Fig. 2) and is purified by passing through the three wash bottles L_1, L_2 and L_3 (containing in L_1 and L_2 an aqueous solution of potassium hydroxide and pyrogallol, and in L_3 concentrated sulphuric acid), and the three tubes, M_1, M_2 and M_3, containing respectively soda-lime, calcium chloride and phosphorus pentoxide. The hydrogen pressure is shown by the manometer N.

With this preliminary survey of the apparatus, it will be easy to follow the details of a series of measurements. Operations are begun by drawing liquid ammonia into the Dewar tubes, D, F and H. The valve of A is then opened and methylamine is distilled into the receptacle D, whence it is run through the stop-cock, S^4, into the conductivity cell E, and thence, for the purpose of washing the cell and the connecting tubes,—a portion through the tube, E^3, and the stopcocks, S^5, S^6, S^9, and S^{10}; the remainder through the tube, E, and the stopcocks, S^7, S^8, S^9 and S^{10}, —to the cell, F. Fresh solvent is then run into the conductivity cell in sufficient quantity to cover well the bottom of the cell, after which a weighed quantity of the solute, contained in the platinum spoon, E^9, is introduced through the tubulure, E^{10}. Any particles of the solute remaining attached to the spoon or to to the sides of the tube, E^6. are then washed into the cell by drawing additional methylamine from the receiver, D. The introduction of solvent is continued until the glass pointer, E^4 is just submerged. The solution is then stirred by means of a stream of hydrogen through the stopcocks, S^9, S^8, S^7, and the capillary tube, E, until the solution is homogeneous and the surface of the solution is adjusted accurately on the pointer. The passage of hydrogen through the solution and thence by way of the stopcock, S^6 to the receiver, H, carries methylamine vapor with it, thus enabling the operator to bring about the desired adjustment to the pointer. Since the capil-

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lary tubes, E and E^3, have an appreciable volume, the adjustment of the surface of the solution to the pointer must take place with the stopcocks, S^5 and S^7, set to give gaseous connection between these and the neck of the cell at E. The level of the solution within the capillaries will then come into equilibrium with that of the contents of the cell. Corrections for difference in capillarity between methylamine and water, which latter was used in calibrating the cell, have not been made. The resistance of the solution between the electrodes, E, is then measured by the familiar method of Kohlrausch, connection with the exterior being made through the tubes, E^3, filled with mercury. An aliquot part of the solution is then removed by turning hydrogen under pressure on to the surface of the solution through S^6, after setting the stopcocks S^5, S^8, S^9 and S^{10}, to deliver into the cell, F and allowing the solution to flow out until the tip of the "J" tube, E^5, is just uncovered. Fresh solvent is then introduced, and the operations described above are repeated until the desired dilution is reached.

The Solvent.—The methylamine used in this investigation was a part of a kilogram obtained from Kahlbaum.[1] It was purified by distillation after long contact with metallic sodium to remove any water and ammonia, which might have been present. No tests were made to prove the purity of the solvent, although its essential purity is to be assumed from the observed constancy of its boiling point[2] and the high specific conductivity of the purified liquid. Methylamine of a specific conductivity, $\kappa = 0.7 \times 10^{-6}$ to 1.2×10^{-6}, was easily obtained in the cell of the conductivity apparatus. No attempt has been made to determine the conductivity of the purest methylamine.

Constants and Units.—The units of Kohlrausch have been used.[3] The resistance capacity of the cell at 20.3° was found by means of a fiftieth normal solution of potassium chloride[3] to be 0.1886 Kohlrausch units.

The volumes of the conductivity cell, determined by weighing at 16°, the amount of water required to fill the cell to the respective glass pointers, are for the points E^3 and E^4, 3.92 cc. and 7.83 cc. respectively.

Numerical Results.—In the following tables are given the results of measurements on the five substances studied. The dilutions are expressed in liters per gram molecule, and are denoted by $\varphi/1000$. The molecular conductivities are denoted by the symbol Λ.

TABLE 1.—*Potassium Iodide.*

$\phi/1000$	Λ	$\phi/1000$	Λ
21.8	12.2	174.	17.9
43.5	12.2	348.	23.4
87.0	14.0		

[1] The purchase of this methylamine was made possible by a grant from the Trustees of the Bache Fund, to whom acknowledgment is here made.

[2] Cf. Gibbs, This Journal, 27, 859.

[3] Kohlrausch and Holborn: Leitfähigkeit der Elektrolyte, p. 77.

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TABLE 2.—*Potassium Iodide.*

13.5	13.1	428.	24.4
27.0	12.4	856.	32.7
53.9	12.6	1710.	44.2
107.5	14.4	3420.	64.5
214.5	18.4		

TABLE 3.—*Acetamide.*

12.1	0.031	11.8	0.030
5.9	0.028		

TABLE 4.—*Benzenesulphonamide.*

29.6	0.56	59.1	0.74

TABLE 5.—*Metanitrobenzenesulphonamide.*

16.8	5.64	33.5	5.40

TABLE 6.—*Metanitrobenzenesulphonamide.*

13.4	5.15	106.6	6.88
26.7	4.81	213.0	8.73
53.4	5.40	425.5	15.5

TABLE 7.—*Silver Nitrate.*

0.66	25.9	10.5	22.1
1.32	35.3	21.1	19.6
2.68	30.8	42.1	19.4
5.28	26.4		

TABLE 8.—*Silver Nitrate.*

0.61	27.0	38.8	17.8
1.22	33.3	77.5	22.2
2.44	31.5	154.8	26.2
4.87	26.9	309.0	33.3
9.72	22.8	618.0	44.8
19.4	20.4		

TABLE 9.—*Silver Nitrate.*[1]

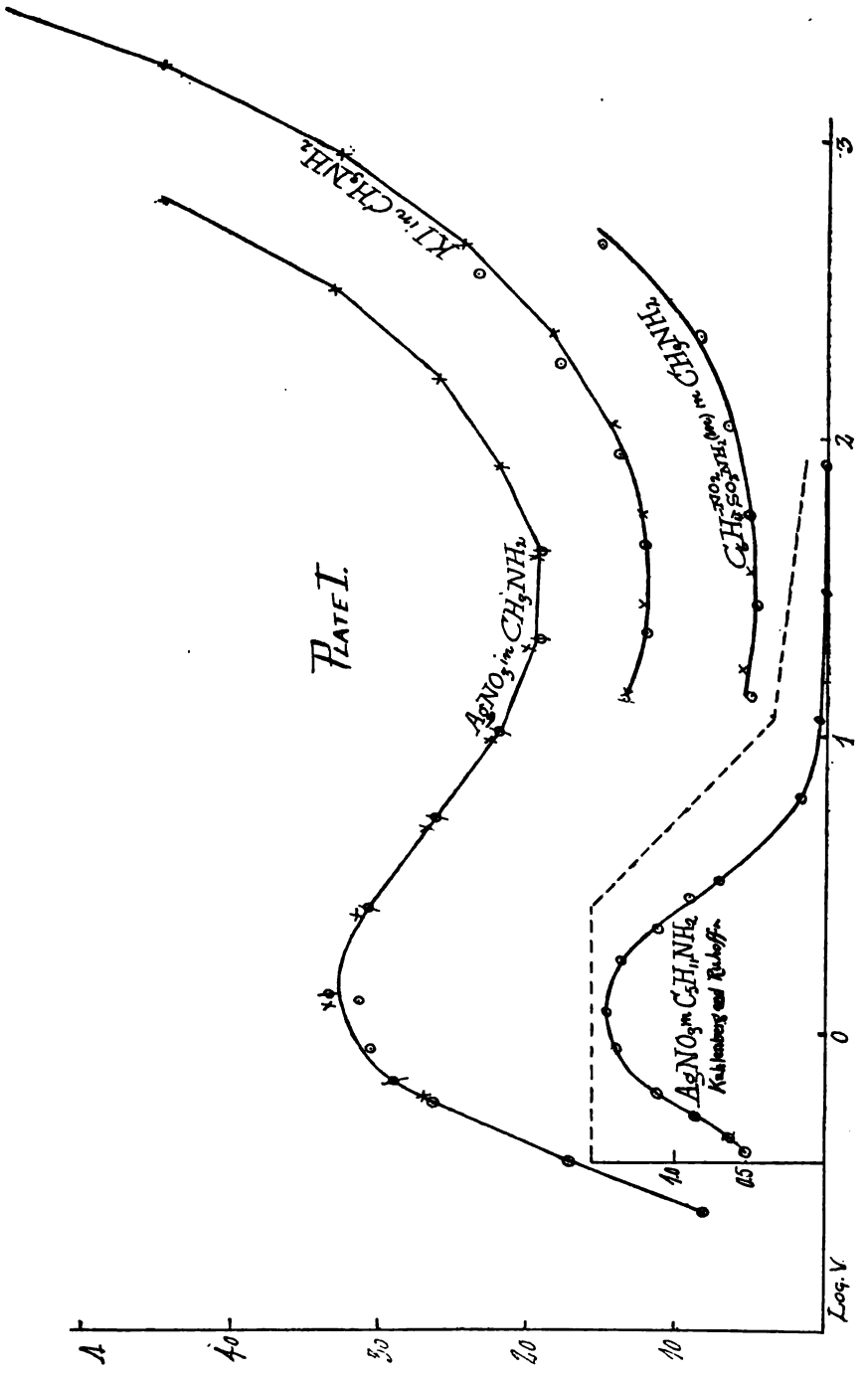
0.244	8.14	0.868	30.4
0.362	17.2	1.28	31.4
0.581	26.4		

Graphical Representation of the Results.—In the accompanying plate are plotted the results obtained for silver nitrate, potassium iodide and metanitrobenzenesulphonamide in methylamine together with a curve representing the behavior of silver nitrate in amylamine.[2] The molecular conductivities are plotted as ordinates, the logarithms of the dilutions as abscissas. The logarithms of the dilutions rather than the dilutions themselves, or even the cube roots of the dilutions, are used for the reason that this method gives a better distribution of points in the more concentrated solutions.

[1] This set of measurements was made with a cell of the following constants: Volume to point 1, 2.98 cc.; point 2, 4.43 cc.; point 3, 7.11 cc.; point 4, 10.63 cc.; point 5, 15.66 cc. The cell constant was, 0.1905.

[2] Kahlenberg and Ruhoff, J. Phys. Chem., 7, 254.

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Discussion of Results.—It has been noted that certain non-aqueous solutions not infrequently exhibit the phenomenon of diminishing molecular conductivity with increasing dilution.[1] In other cases[2] the molecular conductivity falls to a minimum, after which with further dilution it rises continuously. Lewis[3] has found that the molecular conductivity of potassium iodide in liquid iodine at first increases with the dilution to be followed by a striking fall. A similar behavior of silver nitrate in amylamine has been observed by Kahlenberg and Ruhoff[4].

As the curve for silver nitrate in methylamine in the above plate shows, the authors have now found that a methylamine solution of silver nitrate combines the earlier observed effects with those described by Lewis. The behavior of Lewis' solution is represented by the first portions of our curve, that of the solutions studied by Kablukoff, Euler, and MacIntosh and Archibald, by the middle portions, while the latter portions coincide in their graph with the more dilute solutions of the cyanides in liquid ammonia as observed by Franklin and Kraus.

What, in the light of the theory of electrolytic dissociation, the explanation for the unique behavior of our methylamine solutions may be, it is difficult to say. Steele, McIntosh and Archibald[5] explain the behavior of solutions in the liquefied halogen acids by assuming the formation of polymeric forms of the solute, or by the union of more than one molecule of the solute with more or less of the solvent to form aggregates which are in equilibrium on the one hand with their original constituents and on the other with the products of their electrolytic dissociation. They show that by this hypothesis they may explain the observed falling molecular conductivity with increasing dilution. It is not obvious, however, how this conception may be extended to account for the maximum and minimum of our curve, or to follow the curve to concentrations above and below these points.

According to Walden[6] the normal conductivity curve is shown by solutions which are essentially physical mixtures, while the abnormal curves are the result of chemical changes either in the solvent alone or between the solvent and solute. He accordingly explains the increase of conductivity of certain relatively concentrated solutions in acetaldehyde on the assumption that under these conditions, the normal dissociation obscures

[1] Kablukoff: Z. physik. Chem., 4, 429; Euler, Ibid., 28, 623; Kahlenberg and Ruhoff, J. phys. Chem., 7, 254; Platinkoff, Z. physik. Chem., 48, 220; Sakur, Ber., 35, 1242; Walden, Z. physik. Chem., 43, 385, and 54, 141; McIntosh and Archibald, Phil. Trans. A., 205, 120.

[2] Walden, loc. cit. Franklin and Kraus, This Journal, 27, 215.

[3] Proc. Acad. Arts and Sci., 41, 419.

[4] Loc. cit.

[5] Loc. cit., p. 148.

[6] Z. physik. Chem., 54, 145.

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the chemical effects. The molecular conductivity therefore increases with the dilution and reaches a maximum. On further dilution, "aldolytic" decomposition, giving rise to poorer electrolytes, becomes conspicuous with the result that continued dilution brings with it a depression of the molecular conductivity to a minimum beyond which the normal dissociation of the products of aldolysis gives a conductivity curve rising with further increase of the dilution, in the familiar manner, to a maximum. While such an hypothesis may account for the observed behavior of aldehyde solutions, it is not clear how a similar explanation may be applied to solutions of silver nitrate in methylamine. In any event, in view of the behavior of silver nitrate in ammonia solutions,[1] it seems impossible to assume "aminolytic decomposition" in these methylamine solution.

Lewis[2] has proposed an hypothesis, one also touched upon by Franklin and Kraus,[3] which, as it seems to the authors, may account for the observed behavior of our solutions. The hypothesis, modified to include the present case, may be outlined as follows: Salts dissolved in a weak ionizing solvent may be expected to give solutions in which the self-ionization of the salt shows itself conspicuously.[4] Methylamine, such a solvent, dissolves silver nitrate abundantly, forming solutions, which, when very concentrated, are possessed of a high degree of viscosity. The conductivity of the most concentrated solutions, in that they approach the condition of the melted salt, is therefore, for the most part, due to the autoionization of the salt. As the solution is diluted its viscosity diminishes rapidly with the result that the increasing speed of the ions, which has been shown by Walden[5] to accompany diminishing viscosity, more than counteracts the effect of diminishing self-ionization which may be assumed to accompany the dilution, and which of itself would cause a diminution of the conductivity. The observed conductivity therefore increases. The viscosity, however, falls off at a rapidly diminishing rate as the dilution increases, so that after a time the opposing effects of viscosity and self-ionization balance each other, when a maximum of molecular conductivity is reached. From this point on, for a time, increasing dilution is most conspicuous in its effects on the autoionization of the salt. The rate at which the autoionization diminishes becomes smaller as the dilution continues to increase with the result that, beyond a certain point, the dissociating action of the solvent becomes conspicuous as the curve passes through the minimum and then ascends after the familiar manner of salts in aqueous solution.

[1] Cf. Franklin, This Journal, 27, 833.
[2] Proc. Am. Acad. Arts and Sci., 41, 427.
[3] This Journal, 27, 216.
[4] Obviously, this cannot be true in all cases. Cf., for example, Kahlenberg's solutions of copper oleate in benzene (J. phys. Chem., 6, 1).
[5] Z. physik. Chem., 55, 207.

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This seems to give a fairly satisfactory qualitative explanation of the conductivity relations of silver nitrate in methylamine solution. It will be noticed that potassium iodide and metanitrobenzenesulphonamide in methylamine, and the cyanides of the heavy metals in liquid ammonia,[1] give very similar curves, excepting that they have not yet been continued into the more concentrated solutions.

Summary.

It is shown that methylamine, a liquid of rather wide solvent power, is also a good electrolytic solvent.

The electrical conductivity of a short series of substances in methylamine have been measured.

Silver nitrate in solution in methylamine has been found to give a unique conductivity curve for which a tentative explanation is offered.

STANFORD UNIVERSITY,
California, June, 1907.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ADELBERT COLLEGE.]

THE VAPOR PRESSURE OF SULPHUR AT LOW TEMPERATURES.

BY HIPPOLYTE GRUENER.

Received August 12, 1907.

Matthies[2] has recently determined the vapor pressure of sulphur at temperatures between 200° and 400°. The vapor pressure at lower temperatures, varying from 50° to 120°, was determined by the writer by passing known amounts of a dry inert gas over sulphur heated to the desired temperature. The sulphur volatilized was collected on the walls of a cold tube and from its weight the pressure was calculated. Independently a series of determinations was undertaken at the boiling point of water. The vapor pressure in these determinations was calculated from the amount of sulphur volatilized with known amounts of water. Although the agreement among the individual determinations of this second method was not very close, the mean result was the same as that obtained by the first method.

For the first method sulphur was enclosed in a U-tube with ground connections. This enabled the exit tube, on the cold walls of which the sulphur was deposited, to be removed and weighed. The loss of weight upon heating the tube in a current of air gave the weight of the sulphur. The sulphur was used in the form of small crystals, obtained by stirring melted sulphur as it solidified, and this form was well adapted to the purpose. The total length of the column was 20 to 25 cm., its diameter 1.5 cm., and its weight about 25 g. The U tube was placed in a copper box surrounded by water or a solution of calcium chloride. The temperature was maintained constant by a gas regulator, except at 100°,

[1] This Journal, 27, 215.

[2] Phys. Z., 7, 395.

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when it was maintained by the boiling of the water. The variations of temperature were averaged by frequent readings, it being assumed that for small intervals the curve of the vapor pressure is a straight line.

The gases used were carbon dioxide, hydrogen, and at the lowest temperatures, air. Hydrogen was used only in one determination, namely at 100°; there was no trace of any reaction with the sulphur, and the results were the same as those obtained with carbon dioxide. Air was used with determinations at 100° and below, but only the determinations at the lowest temperatures are included among the main results. The others will be discussed separately. The flow of the gas was regulated by passing it through a capillary tube of the proper proportions and by the pressure produced in the generators. The carbon dioxide and hydrogen were prepared in the usual way and dried with sulphuric acid. The determinations were frequently made in pairs, which fact facilitated the operations and supplied a test for the saturation of the gas, for in each pair of determinations all the conditions were the same, except the rate of passing the gas. The amount of gas was measured by an experiment meter at the end of the system.

The saturation of the gas was established in two ways. By one method two U-tubes, filled with sulphur, were connected in series and with all the other conditions the same as in the regular experiments, the loss of sulphur was investigated. The results were as follows:

TABLE 1.

	Amount of Gas. L.	Duration of Expt. Days.	Rate of Gas. L per D.	Loss of S. 1st tube. grams.	Loss of S. 2nd tube. grams.	S. deposited at end. grams.
A	103	7.5	14	0.0096	0.0001	0.0096
B	175	7.5	23	0.0165	0.0003	0.0159

In each case the loss of sulphur, within the limits of error of the experiment, was confined to the first tube.

Saturation was further assured by varying the rate of the flow of the gas within somewhat wide limits, when no corresponding wide limits of variation in the loss of sulphur was observed, as shown in Table 2. The larger or smaller results shown in this table are seen to have no dependence upon the different rates of passing the gas.

TABLE 2.

No. of Expt.	Temp. C.	Duration, Days	Am't. Gas. L.	Rate, L. per D.	Deviation of rate from mean. Per cent.	Corresponding vapor pressure. mm.	Deviation of vapor pressure from mean. Per cent.
7 A	100°	9.8	207	21.1	4.5+	0.0076	2.0+
B	100°	9.8	173	17.6	12.8—	0.0074	0.6—
C	100°	12.7	231	18.2	9.9—	0.0074	0.6—
D	100°	12.7	200	15.7	22.3—	0.0075	0.6+
E	100°	5.8	141	24.3	20.3+	0.0074	0.6—
F	100°	5.8	140	24.2	19.8+	0.0074	0.6—
				Mean 20.2		Mean 0.00745	

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The same check was applied to most of the other determinations. When this was omitted, reliance was placed on the similarity to comparable determinations when the check was applied. Determinations 3, 4, 5, 6 and 10 were thus checked as shown in Table 3, and the differences in the results obtained, are either negligible or of such irregularity of amount and sign, that they cannot be attributed to lack of saturation.

TABLE 3.

No. of Expt.	Temp.	Duration Days	Am't of gas L.	Rate per day L.	Deviation from mean rate. Per cent.	Corresponding vapor pressure mm.	Deviation of vapor pressure from mean. Per cent.
3 A	70°	4.8	177	37	23+	0.00045	5—
B	70°	4.8	181	38	27+	0.00050	6+
C	70°	11.8	183	15	50—	0.00047	1—
4 A	80°	5.7	148	26	24+	0.0010	10—
B	80°	5.7	146	26	24+	0.0011	0
C	80°	10.9	115	11	48—	0.0012	10+
5 A	90°	3.7	83	22	17+	0.0030	4+
B	90°	3.7	81	22	17+	0.0030	4+
C	90°	11.9	140	12	34—	0.0026	8—
6 A	95°	5.0	129	26	24+	0.0044	3+
B	95°	5.0	108	22	4+	0.0041	4—
C	95°	8.0	120	15	28—	0.0043	1+
10 A	110°	5.0	72	14	15—	0.0137	1+
B	110°	5.0	95	19	15+	0.0134	1—

The rates (liters per day) in other determinations were :

Expt. 1, 50°, rate = 46 ; Expt. 2, 55°, rate = 35 ; Expt. 9, 105°, rate = 13 ; Expt. 11, 120°, rate = 11.

It is certain from the following considerations that the volatilized sulphur was completely redeposited in the exit tube.

1. The temperature of the warmest portion of this tube was 40°, and of the colder portion 30°. The vapor pressure corresponding to this temperature is 0.00001 mm. involving a maximum loss of 0.03 milligram for each determination.

2. The layer of sulphur was deposited within narrow limits, with no sign of it in the more distant portions of the tube. When a bend in the tube was kept in ice-water during the entire progress of one determination, there was noticed a just discernible breath of sulphur, far too small in amount to affect the results.

The determinations of the vapor pressure are shown in Table 4.

More attention was paid to the vapor pressure at 100° than to that at any other temperature. This was determined for prismatic sulphur by four determinations with carbon dioxide, and two determinations with hydrogen. The prismatic condition was assured by crystallizing the sulphur as above indicated, and introducing it into the chamber heated to 100° within 30 minutes from the time of its cooling. The six determi-

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TABLE 4.

No. of Expt.	Gas used	Temp.		Volume of gas at meter.	Temp. at meter.	Amount of Sulphur volatilized. grams.	Calculated vapor-pressure. mm.	Temp. in round nos.	Vapor-pressure corresponding. mm.	Mean. mm.	Vapor-pressure calculated from formula. mm.
1	Air	48.6		199.53	18.0	0.00021	0.00007	50°	0.00008		0.00008
2	Air	56.1		266.02	17.2	0.00055	0.00015	55°	0.00013		0.00012
3	CO_2	68.8		183.06	19.0	0.00110	0.00043	70°	0.00047		0.00049
4	CO_2	81.1		114.57	15.5	0.00216	0.0013	80°	0.0012		0.0012
5	CO_2	91.0		139.73	14.8	0.0058	0.0029	90°	0.0026		0.0030
6	CO_2	94.9		119.52	15.0	0.0072	0.0042	95°	0.0043		0.0047
7 A	CO_2	99.7	Prismatic Sulphur	207.10	23.4	0.0212	0.0074	100°	0.0076		
B	CO_2	99.7	Prismatic Sulphur	172.61	22.8	0.0173	0.0072	100°	0.0074		
C	CO_2	99.6	Prismatic Sulphur	230.86	22.7	0.0231	0.0072	100°	0.0074		
D	CO_2	99.6	Prismatic Sulphur	199.74	22.1	0.0203	0.0073	100°	0.0075	0.00745	0.00745
E	H	99.8	Prismatic Sulphur	140.90	23.3	0.0142	0.0072	100°	0.0074		
F	H	99.8	Prismatic Sulphur	140.20	22.5	0.0142	0.0072	100°	0.0074		
A	CO_2	99.7	Rhombic Sulphur	242.88	23.0	0.0235	0.0069	100°	0.0071		
B	CO_2	99.7	Rhombic Sulphur	173.05	22.3	0.0171	0.0071	100°	0.0073	0.0072	
9	CO_2	104.4		73.76	21.3	0.0103	0.0100	105°	0.0104		0.107
10 A	CO_2	109.8		71.83	21.4	0.0136	0.0135	110°	0.0137		
B	CO_2	109.8		95.05	20.8	0.0176	0.0132	110°	0.0134	0.0136	1.0154
11	CO_2	120.5		55.64	21.3	0.0233	0.0351	120°	0.0339		0.0320

Calculated vapor pressure for 20° = 0.000005; for 30° = 0.000013; for 40° = 0.00003; for 60° = 0.00020.

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nations agreed fairly closely, ranging from 2 per cent. above to 0.6 per cent. below the mean.

Under experiment 8 are given the results for rhombic sulphur. These determinations were made with crystals like those used in the above experiment, converted into the rhombic form by standing for days. The results may, however, be taken only as qualitative, since the point in time was not determined when the temperature of 100° was influential in reproducing the prismatic form.

The values for the vapor pressure for the temperatures above, 100°, are probably not so accurate as for this temperature, inasmuch as the apparatus was not so well suited for the purpose. The bath surrounding the warm chamber consisted of a calcium chloride solution. At 120° the sulphur was placed in a tube about 30 cm. long and inclined at a small angle, so that the gas passed in slow bubbles through the liquid sulphur.

When the values of the logarithms for the vapor pressure at and below 100° are plotted, they lie near a straight line whose prolongation, however, does not include the higher values. From this a general expression may be obtained for the vapor pressure of sulphur:

$$p = a\, b^t$$

For temperatures from 50° to 100°, log. $a = \overline{7}.9225$, log. $b = 0.0395$, t = temperature centigrade. For temperatures somewhat above 100°, log. $a = \overline{3}.8725$, log. $b = 0.0316$, t = temperature centigrade — 100. The values for the vapor pressures thus calculated are given in the last column of Table 4.

It seemed desirable to try another gas besides carbon dioxide and hydrogen. Dry air was used in a series of determinations at 100° and below. It was evident from preliminary trials that the sulphur was oxidized only slightly, if at all, and this was confirmed by the results shown in Table 5. These determinations were a repetition of those of Table 4, except that air was used instead of carbon dioxide.

TABLE 5.

No. of Expt.	Corrected temp.	Amount of sulphur deposited in exit tube for 100 L. gas. g. for CO_2	for air.	Corresponding vapor pressure. for CO_2.	for air.	Amount of sulphur oxidized (as determined by amount of SO_2).
3	70°	0.00057	0.00057	0.00047	0.00047	very slight
4	80°	0.0014	0.0012	0.0012	0.0011	very slight
5	90°	0.0030	0.0034	0.0026	0.0030	
6	95°	0.0048	0.0048	0.0043	0.0043	very slight
7	100°	0.0083	0.0078	0.0075	0.0071	0.00033 g.

The results show that at 100°, the oxidizing action of dry air upon sulphur in this form is very slight, yet it is enough to vitiate the results. (The odor noticeable when sulphur is heated to this temperature is that of the volatilized sulphur, not of sulphur dioxide.) At temperatures below 100°, the loss cannot be determined, the results being apparently independent of this condition. This was confirmed by submitting sulphur in the same form to the action of dry oxygen at these temperatures

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and determining the sulphur dioxide formed. Only at 100° could an appreciable amount be observed, namely, that corresponding to an oxidation of 0.0001 g. sulphur per day of contact.

During the progress of some experiments recently performed in this laboratory, it was found desirable to know the possible loss of sulphur when water holding it in suspension was evaporated. This suggested a method for determining the vapor pressure of sulphur at 100°. Accordingly, water with sulphur in suspension was boiled, and the steam passed over a column of sulphur in the form of shot. The column was 50 cm. long, 1.5 cm. in diameter, and contained about 100 g. of sulphur. This sulphur column was surrounded by a jacket through which steam was passed to maintain the sulphur at the proper temperature. The steam which had passed over the sulphur column was condensed, and the sulphur contained in the distillate determined. It was weighed as barium sulphate after oxidation with hydrogen peroxide in alkaline solution.

The only guaranty of the saturation of the steam was the uniformity of results obtained, although the rate of passing the steam over the sulphur was varied. The steam escaping from the flask in which the water was boiled with sulphur was evidently not saturated, but when it was passed in addition over this column of sulphur, the results became reasonably uniform. The rate varied in eleven determinations from 4.4 g to 0.6 g. water distilled per minute. If these be roughly divided into those whose rate is greater than 2 g. per minute and those whose rate is less than 2 g. per minute, it developes that the more rapid average 2.3 per cent. above the mean, while the slower average 1.6 per cent. below. There were values, however, in both cases, with the opposite sign. One result, number 9, differed so much from the others that it is not included in the first summary, although no reason is apparent for this discrepancy unless it be that the rate of distillation was slower than that of the other experiments. The results are shown in Table 6.

TABLE 6.

No. of Expt.	Am't water distilled. Grams.	Am't S found. Grams.	Am't S per 100 g. water. Grams.	Deviation from mean. Per cent.
1	127.41	0.0184	0.0145	7.9+
2	132.30	0.0185	0.0140	4.2+
3	122.64	0.0159	0.0130	3.3—
4	141.86	0.0198	0.0139	3.4+
5	54.52	0.0076	0.0139	3 4+
6	116.12	0.0151	0.0130	3.3—
7	83.50	0.0113	0.0135	0.5+
8	30.39	0.0039	0.0130	3.3—
10	40.42	0.0051	0.0126	6.3—
11	94.52	0.0124	0.0131	2.5—
12	65.62	0.0087	0.0133	1.0—
		Mean	0.01344	
9	48.83	0.0053	0.0108	18.0—
		Mean	0.01322	

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The temperature was taken as that of the boiling point of water, 99.3° at the mean barometric pressure, 740.7 m.m., for the days during which the experiment was performed. Number 9 is omitted from the calculations. Using the mean of the other eleven determinations for the calculation, the vapor pressure for this temperature was found to be 0.0070 mm. The vapor pressure calculated from the results of the other method for this temperature is 0.0070 mm., which agrees with this result. If determination 9 be included the vapor pressure calculated is 0.0069, a result not materially different from the other.

Cleveland, Ohio.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY No. 19].

IONIZATION OF WATER AT 0°, 18° AND 25° DERIVED FROM CONDUCTIVITY MEASUREMENTS OF THE HYDROLYSIS OF THE AMMONIUM SALT OF DIKETO-TETRAHYDROTHIAZOLE.

BY C. W. KANOLT.

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1. Plan of the Investigation.

The degree of ionization of water at ordinary temperatures has been determined by a number of different methods—namely (1) from the hydrolysis of sodium acetate[1] as derived from the rate at which it saponifies an ester,[2] and from that of aniline acetate[3] as derived from conductivity measurements[4]; (2) from the rate of saponification of methyl acetate by water itself;[5] (3) from the electromotive force of the alkali-acid hydrogen cell;[6] and (4) from the conductivity of the purest water thus far obtained.[7] Although these entirely independent measurements have all given for the ionization of water values of the same order of magnitude and have thereby furnished one of the most striking evidences of the ionic theory, yet for none of the values so obtained can any considerable percentage accuracy be claimed. It has therefore seemed advisable to make a special study of this constant at ordinary temperatures by the same method that has been employed at higher temperatures by Noyes and Kato and by Sosman,[8] that is, by measuring the increase

[1] Arrhenius, Z. physik Chem., 11, 822 (1893)

[2] Shields, Ibid., 12, 184 (1893).

[3] Arrhenius, Ibid., 5, 19 (1890); Bredig, Ibid., 11, 829 (1893).

[4] Walker, Ibid., 4, 334 (1889).

[5] Wijs, Ibid., 11, 492 (1893).

[6] Ostwald, Ibid., 11, 521 (1893); Nernst, Ibid., 14, 155 (1894); Löwenherz, Ibid., 20, 293 (1896).

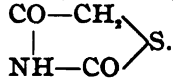
[7] Kohlrausch and Heydweiller, Ibid., 14, 330 (1894).

[8] These articles together with the present one are being published by the Carnegie Institution of Washington.

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in conductance produced by adding to a partially hydrolyzed salt of a weak acid and a weak base an excess of the acid or of the base, whereby the hydrolysis is reduced.

In calculating from such data the ionization of water a knowledge of the ionization-constants of the acid and the base and of the degree of ionization of the salt is also necessary.

The salt selected for this purpose must be sufficiently hydrolyzed to give rise to a marked change in the unhydrolyzed portion of it when the excess of acid or base is added. On the other hand, both the acid and the base of the salt must be strong enough to permit their ionization-constants to be directly and accurately determined by conductivity measurements. An examination of the available substances previously investigated seemed to show that ammonium hydroxide was the most suitable base, and that diketotetrahydrothiazole was the most suitable acid. This acid has also been called dioxythiazole and mustard-oil acetic acid, and has, according to the investigation of Hantzsch[1], the structure[2] . The base has at 25° an ionization-constant of 18.1×10^{-6} and the acid, one of 0.181×10^{-6}, and their salt a hydrolysis of about 4 per cent. as the measurements presented below show. This base is more easily obtained pure than any other base of similar strength; and the acid can be readily prepared in quantity from thiourea and chloracetic acid. It is, however, so weak, that its salt is about ten times as much hydrolyzed as ammonium acetate (which is 0.4 per cent. hydrolyzed at 25°); and yet it is strong enough to have a conductance which can be fairly accurately determined, though it lies near the limit in this respect.

In detail, therefore, this investigation has consisted in the preparation and purification of the diketotetrahydrothiazole and the determination of its ionization by conductivity measurements at 0°, 18°, and 25° at various concentrations, in corresponding measurements with ammonium hydroxide, and in measurements at these three temperatures of the conductance of the salt at 0.02 and 0.05 normal both in water alone and in the presence of about the equivalent amount and half the equivalent amount of the free acid and of the free base in separate experiments. In order to determine the conductance of the completely ionized acid and salt, measurements were also made with the latter at a concentration of 0.002 normal.

2. Preparation of the Substances and Solutions.

The diketotetrahydrothiazole was prepared as described by Volhard[3]

[1] Ber., 20, 3129 (1887).

[2] Even assuming that this substance exists in part in the desmotropic "enol" form, this would make no difference in the values of the ionization of water derived from the study of its equilibria; for the concentrations of the two forms must be under all circumstances proportional to each other.

[3] J. pr. Chem., (2), 9, 6 (1874).

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by heating together thiourea and chloracetic acid in aqueous solution. The product was purified by a large number of crystallizations from methyl alcohol and from water. No boneblack was used. The crystallization from water was continued until the sample was perfectly white and no further change in conductance was produced, as will be shown in section 4. The last crystallizations were made from conductivity water in platinum vessels, and the crystals were filtered out and dried at 100° in a platinum Gooch crucible in purified air. A portion of the product so dried was finely powdered and kept in a desiccator over sulphuric acid for several weeks; it lost only a few hundredths of one per cent. in weight, showing that it was dry. The melting point of the purified sample was found to be 123.4°

The solutions of the acid were always prepared just before the conductance was measured, by dissolving weighed portions of it in a known weight of conductivity water in a Jena flask. The solutions were prepared and transferred to the conductivity vessel in contact with only purified air. The water used for dissolving the acid, and in general throughout this investigation, had at 18° a specific conductance which always lay between 0.15 and 0.60×10^{-6} reciprocal ohms. The solutions of the acid, even when kept for several hours in the conductivity-vessel, showed a change in conductance of not more than 0.1 per cent.

The ammonium hydroxide solution used was approximately 0.1 normal made by diluting with conductivity water a special sample of strong ammonia water (spec. grav., 0.90) furnished by the Baker & Adamson Chemical Co. and certified to be free from amines, carbonates, and silicates. The solution was titrated by running a slight excess of it directly into a known weight of standard hydrochloric acid, and running back to the end point with hydrochloric acid with the help of methyl orange. The solutions were all measured by weight, not by volume. The hydrochloric acid was itself standardized by precipitating a known weight of it with silver nitrate and weighing the silver chloride. The solution was kept in a two-liter "non sol" bottle (furnished by Whitall, Tatum & Co.). To protect it from evaporation and contamination it was connected through another bottle of ammonium hydroxide solution of the same strength with a long soda-lime tube through which air was admitted when samples were withdrawn. The solution was transferred through delivery tubes into the conductivity vessel or into a Jena flask in which it was diluted or mixed with the acid solution, in contact with only purified air. In order to use comparatively fresh solutions for the measurements, a new stock solution was prepared in the same way in the course of the experiments, so that the solution employed was never more than ten days old. Determinations of the alkaline strength showed that during this period the change in it was less than 0.1 per cent. The con-

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ductance of this solution was found to be substantially identical with that of one prepared from liquid ammonia by Mr. R. B. Sosman.

The solutions of the salt, both alone and with an excess of acid or base, were prepared by introducing into a Jena flask, provided with a perforated ground-glass stopper and filled with purified air, a weighed quantity of the solid acid, and then introducing without opening the flask the proper quantity of conductivity water and of the stock ammonium hydroxide solution to produce as nearly as possible any desired round concentrations. These were in general attained within 0.1 or 0.2 per cent., but the exact concentration was always considered.

The content by weight of the various solutions obtained as above described was reduced to volume concentration by means of the density of the solution, which in the case of the acid or salt solutions was calculated from the densities of the solid acid and of the water or ammonium hydroxide solution, under the assumption that no change in the total volume occurs on mixing.[1] The concentration given in the tables below is always that at the temperature of the measurement.

The atomic weights used were those referred to oxygen as 16.00 as given in the report of the International Committee for 1906[2] All weights were corrected for the buoyancy of the air.

3. Apparatus and Method.

The conductivity measurements were made with a slide-wire bridge by the usual Kohlrausch method. The slide-wire was calibrated and the resistance coils were compared with each other. The conductivity vessel used was one of pipette form devised by Mr. G. A. Abbott in this laboratory. It is shown in the figure. It has the advantages that the solution can be introduced into it and kept in it entirely out of contact with the air, that the electrodes are fully protected against change in position, and that the vessel can be entirely immersed in the thermostat. The capacity of the vessel was about 25 cc.; and the vertical electrodes were about 2 cm. square and 1.3 cm. apart. The electrodes were used unplatinized in the measurements with the acid, so as to reduce contamination; but were platinized in the measurements with better conducting base and salt. The conductance-capacity of the vessel was determined by measuring in it (when unplatinized) a freshly prepared 0.002136 normal or (when platinized) a 0.0500 normal solution of potassium chloride,[3] and allowing for the conductance of the water employed.

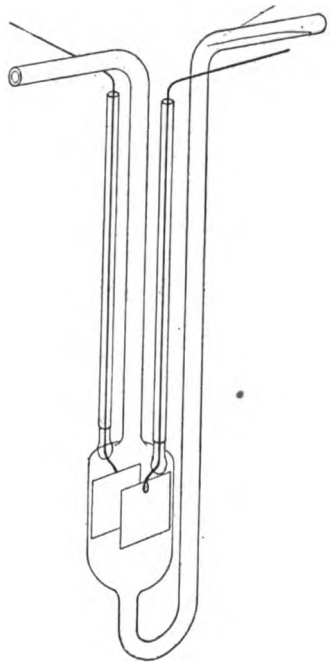
[1] The density of the acid at 25° was found to be 1.673 by weighing a large excess of it in a pycnometer under its saturated solution. That there was in fact no appreciable volume-change on mixing was shown by direct measurements of the density of known solutions of the acid and of its salt.

[2] See this Journal, 28, 1 (1906).

[3] The actual conductances of these solutions in the vessel after allowing for the conductance of the water were 0.0015095 and 0.03256 reciprocal ohms at 18°, which correspond to conductance-capacities of 0.17861 and 0.17775, respectively, using Kohlrausch and Maltby's equivalent conductance values. The same value was obtained at the end of the measurements as at the start.

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The vessel was immersed in well-stirred baths whose temperature was kep constant within 0 .01° by thermostats. That, at 0° was maintained by a mix



ture of water and finely crushed ice in large proportion. The thermometers used were compared with the laboratory standard.

The final bridge reading was not recorded until it had become constant, which required 15-30 minutes. It then remained constant, even over night, in almost all cases, but with a few solutions containing the salt with an excess of ammoninm hydroxide there was a slight progressive increase in conductance, for which a small correction (never more than 0.25 per cent.) was applied, depending upon the time which had elapsed before the reading and upon the temperature to which the cell had been exposed.

4. The Conductivity and Ionization-Constants of Ammonium Hydroxide and Diketotetrahydrothiazole.

Tables 1 and 2 contain the results of the conductivity measurements with ammonium hydroxide and with diketotetrahydrothiazole. The first column gives the temperature; the second, the date; the third, the concentration in equivalents per liter of solution at the temperature of the measurement; the fourth, the conductance in reciprocal ohms as actually measured in the conductivity vessel, multiplied by 10^6; the fifth, the same diminished by the conductance of the water; the sixth,

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the equivalent conductance (Λ) calculated by multiplying the values of the preceding column by the conductance-capacity (0.17861 for the acid and 0.17775 for the base) and dividing by the concentration given in the third column and by 10^3; and the seventh, the ionization-constant (K) calculated from the expression $K = \frac{\Lambda^2 C}{\Lambda_0(\Lambda_0 - \Lambda)}$ and multiplied by 10^6.

The values Λ_0 (the equivalent conductance for complete ionization) used in the calculation of the ionization-constant were derived as follows. That for the OH^- ion at 18° was found to be 173.0 by subtracting Kohlrausch's value[1] for the sodium ion (43.55) from Noyes and Kato's value for sodium hydroxide (216.5). That for the NH^+_4 ion at 18° was found to be 65.4 by subtracting Kohlrausch's value for chloride ion (65.44) from Sosman's value for ammonium chloride (130.9). In this way the value for ammonium hydroxide was found to be 238.4 at 18°. Those for ammonium hydroxide at 0° and 25° were obtained from the corresponding equivalent conductances of the NH^+_4 and OH^- ions at 18° by means of the temperature-coefficients for the conductivities of these ions derived by Kohlrausch.[2] The values so obtained are $\Lambda_{NH_4} = 39.3$, $\Lambda_{OH} = 117.7$

TABLE I.—EQUIVALENT CONDUCTANCE AND IONIZATION OF DIKETOTETRAHYDROTHIAZOLE.

Temperature.	Date 1906	Equivalents per liter	Conductance × 10^6 Observed	Conductance × 10^6 Corrected	Equivalent conductance	Ionization-constant × 10^6. Separate values.	Ionization-constant × 10^6. Mean values.
0	May 24..	0.2503	185.9	184.5	0.1316	0.0710	
	May 21..	0.1251	131.0	129.7	0.1852	0.0703	0.0709
	May 25 .	0.1251	132.3	131.2	0.1873	0.0720	
	May 22..	0.0626	92.9	91.6	0.2613	0.0701	0.0711
	June 1..	0.2503	185.7	184.7	0.1318	0.0712	
	June 2..	0.2503	187.1	186.1	0.1328	0.0723	0.0713
	May 30..	0.1251	130.6	128.9	0.1840	0.0694	
	June 5..	0.0626	94.0	93.2	0.2659	0.0725	
18	May 24..	0.2500	372.5	370.1	0.2644	0.1436	
	May 21..	0.1250	266.1	263.9	0.3770	0.1460	0.1463
	May 25..	0.1250	268.0	266.2	0.3803	0.1487	
	May 22..	0.0625	189.5	187.2	0.5349	0.1471	0.1459
	June 1..	0.2500	371.5	369.9	0.2643	0.1435	
	June 2..	0.2500	373.3	371.6	0.2654	0.1447	0.1455
	May 30..	0.1250	264.8	261.9	0.3740	0.1437	
	June 5..	0.0625	190.8	189.3	0.5410	0.1504	
25	May 24..	0.2496	463.7	460.7	0.3297	0.1780	
	May 21..	0.1248	330.5	328.0	0.4693	0.1804	0.1818
	May 25..	0.1248	333.1	331.0	0.4737	0.1838	
	May 22..	0.0624	237.5	234.8	0.6719	0.1850	0.1814
	June 1..	0.2496	462.6	460.7	0.3297	0.1780	
	June 2..	0.2496	462.6	460.6	0.3296	0.1779	0.1811
	May 30..	0.1248	331.5	328.1	0.4701	0.1810	
	June 5..	0.0624	238.3	236.6	0.6772	0.1876	

[1] Sitzsber. preuss. Akad, Wiss., 1901, 1026-1033.

[2] Ibid., 1901. 10. These coefficients are:

$$(\Lambda_{NH_4})_t = (\Lambda_{NH_4})_{18}\,[1 + 0.0223\,(t - 18) + 0.000079\,(t - 18)^2]$$
$$(\Lambda_{OH})_t = (\Lambda_{OH})_{18}\,[1 - 0.0179\,(t - 18) + 0.000008\,(t - 18)^2]$$
$$(\Lambda_{H})_t = (\Lambda_{H})_{18}\,[1 + 0.0154\,(t - 18) - 0.000033\,(t - 18)^2]$$

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and $\Lambda_{0(NH_4OH)} = 157.0$ at 0°; and $\Lambda_{NH_4} = 75.9$, $\Lambda_{OH} = 194.7$ and $\Lambda_{0(NH_4OH)} = 270.6$ at 25°. The Λ_0 values for the acid at each temperature were obtained from those for its ammonium salt by subtracting the equivalent conductance of the NH^+_4 ion derived as just described, and adding that of the H^+ ion. The Λ_0 values for the ammonium salt were derived from direct conductance measurements which will be presented and discussed in section 5. For the equivalent conductance of the H^+ ion at 18° the value, 315, derived from the measurements of Goodwin and Haskell[1] upon very dilute acid solutions was adopted; while at 0° and 25° the values 224.3 and 348.5, respectively, were obtained from this one at 18° by means of Kohlrausch's temperature-coefficients just referred to.

TABLE 2.—EQUIVALENT CONDUCTANCE AND IONIZATION OF AMMONIUM HYDROXIDE

Temperature	Date	Equivalents per liter	Conductance × 10^6. Observed	Corrected	Equivalent conductance	Ionization-constant × 10^6 Separate values	Mean values
	1906						
0	July 22..	0.09569	1,015	1,014	1.884	13.95	13.91
	July 24..	0.04540	696	695	2.722	13.88	
18	July 22..	0.09557	1,709	1,708	3.177	17.21	17.15
	July 24..	0.04534	1,171	1,170	4.584	17.09	
25	July 22..	0.09542	1,989	1,988	3.703	18.11	18.06
	July 24..	0.04527	1,363	1,362	5.346	18.02	

The measurements of May 30 to June 5, given in Table 1, were made with a sample of the acid obtained by recrystallizing three times from conductivity water with the usual precautions, the material used in these measurements of May 21-25. The agreement of the results with the two samples shows that the material underwent no change in the three crystallizations. Ostwald[2] obtained the value 0.24×10^{-6} for the constant at 25° without using special precautions.

Sosman with solutions prepared both from liquid ammonia and from the pure ammonia water, obtained for the constant of ammonium hydroxide at 18°, as the mean of a large number of determinations at concentrations from 0.01 to 0.1, the value 17.15×10^{-6}, which is identical with that given in Table 2. He obtained the value 17.9×10^{-6} as the means of two determinations at 25°. This value agrees closely with the value 18.06×10^{-6} here presented. Earlier investigators[3] obtained considerably higher results, partly owing to the incomplete elimination of impurities and to the use of other values for complete ionization.

The results given in the tables show that the constants of the two substances do not vary considerably with the concentration. Sosman, using a much greater range of concentration, also found that the variation of the constant for ammonium hydroxide at 18° was very small.

It will be observed that with rising temperature the ionization of the

[1] Physic. Rev., 19, 386, (1904).

[2] Z. physik. Chem., 3, 181 (1889).

[3] Bredig, Z. physik. Chem., 13, 294, (1894). Davidson, Ber., 31, 1612 (1898). Hantzsch and Sebaldt, Z. physik. Chem., 30, 296 (1899).

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acid increases very rapidly, and that that of the ammonium hydroxide also increases, but to a much smaller extent.

No reliable estimate of the accuracy of these constants can be made. It seems, however not improbable that the equivalent-conductance values for the acid may be too high by one per cent., owing to the effect of impurities; and also that its equivalent-conductance values for complete ionization may be in error by one per cent. at 18° and 25°, and by even 2-3 per cent. at 0°. Under these assumptions the error in its ionization-constant may be 3-4 per cent. at 18° and 25°, and 5-7 per cent. at 0°. In the case of ammonium hydroxide, although the values of the equivalent conductance at the higher concentrations are probably somewhat more exact than those for the acid, yet there is an even greater uncertainty in the values for complete ionization, so that the ionization-constants are probably of the same order of accuracy.

5. Conductivity and Hydrolysis of the Ammonium Salt of Diketotetrahydrothiazole.

The data relating to the conductivity of the pure ammonium salt are presented in Table 3, which is arranged like Tables 1 and 2 except that the specific conductance is given in addition to the equivalent conductance.

TABLE 3.—CONDUCTANCE OF THE AMMONIUM SALT OF DIKETOTETRAHYDROTHIAZOLE.

Temperature	Date 1906	Equivalents per liter	Conductance × 10^6 Observed	Corrected	Specific conductance × 10^6	Equivalant conductance
0	July 28..	0.05005	14,424	14,423	2,563.6	51.22
	July 29..	0.04997	14,401	14,400	2,559.4	51.22
	July 12..	0.020047	6,015	6,013	1,068.8	53.32
	July 14..	0.020035	6,016	6,014	1,069.3	53.37
	Aug. 3..	0.002143	686.5	685.2	121.8	56.82
18	July 28..	0.04999	22,895	22,893	4,069	81.40
	July 29..	0.04991	22,828	22,826	4,057	81.30
	July 12..	0.020021	9,566	9,563	1,700.0	84.91
	July 14..	0.020010	9,562	9,559	1,699.1	84.91
	Aug. 3..	0.002141	1,092.2	1,090.0	193.7	90.50
25	July 28..	0.04992	26,408	26,406	4,694	94.03
	July 29..	0.04983	26,355	26,353	4,684	94.00
	July 12..	0.019992	11,044	11,041	1,962.6	98.17
	July 14..	0.019979	11,033	11,030	1,960.0	98.16
	Aug. 3..	0.002137	1,265.6	1,263.0	224.5	105.04

It will be seen that the values of the equivalent conductance at about the same concentration, which were determined with solutions made up separately from the solid acid and the stock ammonium hydroxide solutions, agree in every case within about 0.1 per cent.

For the purpose of facilitating the subsequent calculation of the hydrolysis, the specific conductance L has been expressed as a concentra-

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tion-function of the form $C = \alpha L + \beta L^{3/2}$ which corresponds to the van't Hoff function $(C\Lambda)^{3/2} = KC(\Lambda_0 - \Lambda)$, which is known to express approximately the variation of the equivalent conductance Λ with the concentration C in the case of neutral salts. As this equation is to be used only for interpolation for a small distance from the values from which it is derived, any possible inaccuracy in the assumed form of the function could not introduce a significant error. Using the conductance values at 0.02 and 0.05 normal as the basis, the corresponding numerical equations are:

$$C = 17.330\ L + 43.34\ L^{3/2} \text{ at } 0°$$
$$C = 10.832\ L + 22.95\ L^{3/2} \text{ at } 18°$$
$$C = 9.373\ L + 18.45\ L^{3/2} \text{ at } 25°$$

Table 4 contains the data for the ammonium salt in the presence of an excess of the free acid or base. The first five columns are self-explanatory.

The sixth column contains the uncorrected specific conductance $\times 10^6$ of the solution in reciprocal ohms obtained by multiplying the observed conductance by the conductance-capacity and by 10^6.

The seventh column contains the corresponding specific conductance corrected by subtracting that of the water and in some cases the small estimated increase due to progressive contamination during the period of the measurement (see section 3).

The eighth column headed "Salt in solution" contains the same values after correcting them for the specific conduct of chetane ionized ammonium hydroxide, when this was present in excess. (The conductance due to the ionized acid when it was in excess was entirely inappreciable.) This conductance (L_B) was computed by the equations:

$$C_{OH} = \frac{K_B C_{NH_4OH}}{C_{NH_4}} = \frac{K_B C_B}{C\gamma};$$
$$L_B = 10^3 C_{OH}(\Lambda_{NH_4} + \Lambda_{OH})$$

in which K_B is the ionization-constant for ammonium hydroxide, C_B the excess of it present, and C is the concentration of the salt and γ its degree of ionization.

The ninth column gives the concentration (C_0) at which the salt in water alone has the same specific conductance as that (given in the eighth column) of the salt in the presence of the acid or base; this concentration C_0 was calculated by the empirical relations between C and L given on the preceding page.

The last column contains the values of the percentage hydrolysis ($100\ h_0$) of the salt in water alone at the concentration C_0. These values have been computed by means of the equation:

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$$h_0 = \frac{C_0 - C}{C_0} \cdot \frac{C_B - (C_0 - C)}{C_B - 2(C_0 - C)}$$

in which C represents the concentration of the salt in the mixture and C_B that of the added base (or acid). This equation results from combination of the two equations:

$$C_0(1 - h_0) = C(1 - h),$$
$$(C_0 h_0)^2 = Ch(Ch + C_B),$$

in which h represents the hydrolysis of the salt in the presence of the excess of base (or acid). The first of these, which states that the concentration of the unhydrolyzed portion (which is equal to the sum of the concentrations of the ions and the un-ionized salt) is the same in the two cases, is a consequence of the definition of C_0. The second of these equations is the expression of the mass-action requirement that the product of the concentrations of the free acid and base be the same when the ion-concentrations are the same.

It will be seen from the last column of Table 4 that the values of a. d. (the average deviation of the separate hydrolysis values from the mean) are about 0.10 at 0° and 18°, and 0.15 at 25° for the more dilute salt solution. The deviations for the more concentrated salt solution are much less than these. It is to be remembered in this connection that these hydrolysis values are derived from experiments in some of which an excess of acid, and in others of which an excess of base was present, and in which varying quantities of these were added, and that most constant errors would either have been eliminated in the difference between the measurements with the mixture and the pure salt, or would have shown themselves by producing opposite effects when the acid and base were in excess.

Before calculating the hydrolysis-constant, it is necessary to determine the ionization of the salt at the concentrations in question, and therefore to determine the equivalent conductance Λ_0 for complete ionization. To do this the equivalent conductance of the unhydrolyzed part of the salt has been calculated at the three concentrations at which measurements were made by dividing the specific conductance as given in Table 3 by the concentration of the unhydrolyzed part $C_0(1-h_0)$; and evidently it is to this concentration that the so-obtained values of the equivalent conductance refer. The values for h_0 used at 0.02 and 0.05 normal were the means given in Table 4. The value of h_0 used for the more dilute solution was calculated from these by the mass-action formula given below. From these three values of Λ the values of the three constants n, K, and Λ_0 in the empirical equation, $(\Lambda C)^n = K(\Lambda_0 - \Lambda)C$, were computed. The ionization of the salt was then obtained by dividing the Λ-values by this value of Λ_0.

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TABLE 4.—CONDUCTANCE OF THE SALT WITH AN EXCESS OF ACID OR BASE AND ITS HYDROLYSIS.

Temperature	Date 1906	Milli-equivalents per liter Salt	Acid	Base	Specific conductance × 10^6. Solution. Observed	Corrected	Salt in solution	Concentration (C_0) of salt in water alone	Percentage hydrolysis 100 h_0
0	July 10	20.025		10.95	1,099.8	1,096.8	1,095.5	20.555	2.71
	July 11	20.025		19.78	1,100.6	1,098.4	1,096.0	20.562	2.68
	July 15	20.068	19.96		1,100.5	1,100.3	1,100.3	20.644	2.87
	July 16	20.068	10.13		1,099.8	1,099.5	1,099.5	20.629	2.88
								Mean..	*2.78*
								a. d....	0.09
	July 26	50.06		24.60	2,622.9	2,621.7	2,620.4	51.22	2.37
	July 27	50.06		45.29	2,632.7	2,631.7	2,629.2	51.39	*2.66
	July 30	50.10	49.14		2,622.9	2,622.6	2,622.6	51.27	2.34
	July 31	50.10	24.45		2,623.3	2,623.0	2,623.0	51.27	2.40
								Mean..	*2.37*
								a. d...	0.02
18	July 10	20.000		10.93	1,765.4	1,761.2	17,58.8	20.742	3.82
	July 11	20.000		19.75	1,767.6	1,764.6	1,760.1	20.751	3.76
	July 15	20.044	19.94		1,767.4	1,767.0	1.767.0	20.836	3.95
	July 16	20.044	10.12		1,766.4	1,765.9	1,765.9	20.821	4.04
								Mean..	*3.89*
								a. d....	0.10
	July 26	50.00		24.57	4,200.0	4,194.1	4,191.6	51.63	3.38
	July 27	50.00		45.23	4,215.3	4,210.3	4,205.5	51.80	*3.61
	July 30	50.04	49.08		4,201.3	4.200.9	4,200.9	51.74	3.41
	July 31	50.04	24.43		4,195.9	4,195.5	4,195.5	51.68	3.39
								Mean..	*3.39*
								a. d....	0.01
25	July 10	19.968		10.91	2,042.2	2,039.6	2,036.6	20.784	4.25
	July 11	19.968		19.73	2,047.6	2,045.4	2,040.0	20.818	4.24
	July 15	20.013	19.91		2,050.9	2,050.4	2,050.4	20.921	4.52
	July 16	20.013	10.10		2,047.4	2,046.8	2,046.8	20.884	4.58
								Mean..	*4.40*
								a. d....	0.15
	July 26	49.92		24.53	4,873.9	4,861.7	4,858.7	51.80	3.94
	July 27	49.92		45.17	4,894.7	4,885.1	4,879.4	52.02	*4.22
	July 30	49.96	49.01		4,866.4	4,865.9	4,865.9	51.88	3.85
	July 31	49.96	24.39		4,859.9	4.859.4	4,859.4	51.81	3.86
								Mean..	*3.88*
								a. d....	0.04

*Omitted in the computation of the mean.

Table 5 contains the so-derived values of the equivalent conductance and percentage ionization of the salt. The values of the exponent n were found to be 1.35 at 0°, 1.39 at 18°, and 1.35 at 25°, thus, of about the same magnitude as for ordinary salts. The ionization will also be seen to be about the same as that of other salts of the same ionic type.

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TABLE 5.—EQUIVALENT CONDUCTANCE AND IONIZATION OF THE UNHYDROLYZED AMMONIUM SALT.

Temperature	Equivalents per liter	Equivalent conductance	Percentage Ionization
0	0.04875	52.55	84.5
	0.01950	54.81	88.1
	0.002080	58.5	94.1
	0.00	62.2	
18	0.04816	84.38	85.0
	0.01926	88.22	88.8
	0.002055	94.3	94.9
	0.00	99.3	...
25	0.04782	98.03	83.1
	0.01913	102.54	87.0
	0.002035	110.1	93.4
	0.00	117.9	

From the values of the hydrolysis and ionization given in Tables 4 and 5, the hydrolysis-constant K_H (equal to $\sqrt{\frac{K_W}{K_A K_B}}$) can be readily calculated by the mass-action relation $\frac{h_0}{(1 - h_0)\gamma} = K_H$, in which h_0 represents the hydrolysis of the salt in water alone at any concentration C_0, γ is the fraction of the unhydrolyzed salt $C_0(1 - h_0)$ which exists as ions, and K_W, K_A and K_B are the ionization-constants for water, the acid, and the base respectively. This equation is readily derived by combining the three simple mass-action equations, $C_H C_{OH} = K_W$, $C_H C_A = K_A C_{HA}$, and $C_B C_{OH} = K_B C_{BOH}$, substituting for C_B and C_A the expression $C_0(1-h_0)\gamma$ and for C_{HA} and C_{BOH} the expression $C_0 h_0$, and taking the square root. The values of the hydrolysis constant K_H thus calculated are given in Table 6. The values at the two concentrations will be seen to differ by from 12 to 9 per cent. As those at the higher concentration are influenced to a less extent by impurities and contamination, a double weight has been assigned to them in deriving the final mean values. It is not improbable that these values are still too high but it is unlikely that the error exceeds 5 per cent.

TABLE 6.
THE HYDROLYSIS-CONSTANT FOR THE AMMONIUM SALT.

Temperature	Equivalents per liter	Hydrolysis-constant Separate values	Mean values
0	0.05	0.0287	
	0.02	0.0324	0.0299
18	0.05	0.0413	
	0.02	0.0456	0.0427
25	0.05	0.0486	
	0.02	0.0529	0.0500

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6. The Ionization of Water.

The ionization-constants of water ($K_w = C_H C_{OH}$) can be calculated from the hydrolysis-constants given in Table 6, and the ionization-constants of the acid and base given in section 4. Table 7 contains the values of this constant for water, and also those of its square-root, which last represent the concentration of the hydrogen and hydroxide ion in pure water (in equivalents per liter).

TABLE 7.—THE IONIZATION-CONSTANT OF WATER AND THE HYDROGEN OR HYDROXIDE-ION CONCENTRATION.

Temperature	Ionization-constant $K_w \times 10^{14}$	Ion Concentration $(\sqrt{K_w} = C_H = C_{OH}) \times 10^7$
0	0.089	0.30
18	0.46	0.68
25	0.82	0.91

To compare these results with those previously obtained the various values for the hydrogen-ion or hydroxide-ion concentration in pure water, have been brought together in Table 8.

TABLE 8.—THE HYDROGEN-ION CONCENTRATION ($\times 10^7$) IN PURE WATER. RESULTS OF VARIOUS INVESTIGATORS.[1]

Investigator	Method of Determination	0°	18°	25°
Arrhenius.....	Hydrolysis of sodium acetate by ester-saponification			1.1
Wijs.....	Catalysis of ester by pure water			1.2
Nernst.....	Electromotive force of gas cell.....		0.8	
Löwenherz.....	Electromotive force of gas cell.....			1.19
Kohlrausch & Heydweiller..	Conductance of pure water	0.36	0.80	1.06
Kanolt.....	Hydrolysis.....	0.30	0.68	0.91

It will be seen that the new values are uniformily lower than those of Kohlrausch and Heydweiller, but only by from 16 to 20 per cent. This approximate agreement is of interest not only in indicating the absence of any considerable error in the values of Kohlrausch and Heydweiller, in spite of the somewhat uncertain correction that had to be applied for the impurities in the water; but also in proving that the ionization of water is nearly, if not quite, the same when pure, as it is when an ionized salt is present in it at a concentration of 0.02 to 0.05 normal.

As the most probable values of the hydrogen-ion concentration in pure water it would seem best to adopt for the present the lower ones derived above; for, although it is not impossible that these are in error by as much as 10 per cent., yet it is reasonably certain that the error lies in such a direction as to produce too high rather than too low results. This will be evident when it is considered that the effect of impurities in the

[1] For references to their articles see section 1.

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water or the solutes would be to give rise not only to too high values for the ionization-constants of the acid and base, but also by combining with the excess of either of them added in the hydrolysis experiments, to give too great an increase in the conductance and therefore too great a value for the hydrolysis.

It will be seen from Table 7 that the hydrogen-ion concentration increases with great rapidity with the temperature, being three times as great at 25° as at 0°. It is of interest to calculate from this increase the heat of ionization of water, and to compare its value with that obtained for the heat of neutralization of strong acids and bases. The calculation has been made for the two temperature intervals by the equation log,

$$\log_e \frac{K_2}{K_1} = \frac{Q}{R} \frac{T_2 - T_1}{T_1 T_2},$$

where K_1 and K_2 represent the ionization-constants of water at T_1 and T_2, R is the gas-constant (1.986 cal. per degree), and Q is the heat of ionization of one mol. of water. The value of Q is thus found to be 14,500 calories at 9°, and 14,200 calories at 21.5°. The mean value of the heats of neutralization of potassium and sodium hydroxides by hydrochloric and nitric acids as recently determined by Wörmann[1] is 14,240 calories at 9°

[1] Drude's Ann. Physik., 18, 793 (1905).

and 13,590 calories at 21.5°. The agreement is a surprisingly close one, and shows that the ionization-values at the three temperatures, if affected by errors, must be affected by the same percentage amount.

7. Summary.

In this article have been presented the results of measurements of the conductivity at 0°, 18°, and 25° of ammonium hydroxide, diketotetrahydrothiazole, and of the salt of this base and acid, both alone and in the presence of an excess of the base or acid. From these measurements have been calculated the ionization-constants of the base and acid, the hydrolysis and hydrolysis-constant of the salt, the ionization-constant o water and the concentration of the hydrogen or hydroxide ion in it. The final results may be summarized as follows:

TABLE 9.

IONIZATION-CONSTANTS OF AMMONIUM HYDROXIDE OF DIKETOTETRAHYDROTHIAZOLE, AND OF WATER.

Temperature	Ammonium hydroxide	Ionization-Constants Diketotetrahydrothiazole	Water	Concentration of hydrogen ion in pure water
0	13.91×10^{-6}	0.0711×10^{-6}	0.089×10^{-14}	0.30×10^{-7}
18	17.15×10^{-6}	0.146×10^{-6}	0.46×10^{-14}	0.68×10^{-7}
25	18.06×10^{-6}.	0.181×10^{-6}	0.82×10^{-14}	0.91×10^{-7}

The values for the hydrogen-ion concentration given in the last column are 16 to 20 per cent. lower than those derived by Kohlrausch and Heydweiller from the conductivity of the purest water. From their variation

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with the temperature the heat of ionization of water has been calculated, and found to be in close agreement with the directly measured heat of neutralization of strong acids and bases.

I wish in closing to acknowledge my great indebtedness to Dr. A. A. Noyes, at whose suggestion this work was undertaken, for aid therein.

THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF THE ORGANIC ACIDS IN LIQUID HYDROGEN CHLORIDE AND BROMIDE.

By E. H. Archibald.

Received August 23, 1907.

Introduction.

It has been shown in a previous paper,[1] that the majority of the organic hydroxy bodies dissolve in liquid hydrogen bromide to give solutions which conduct the electric current. It was found however, that, as first pointed out by Steele, McIntosh and Archibald,[2] the behavior of these solutions toward the electric current was very different from that of aqueous solutions of the ordinary electrolytes. As distinguished from these solutions, the molecular conductivity, except in the case of the more dilute solutions, decreased rapidly as the dilution increased. It was found, too, that in a number of cases the specific conductivity decreased with rise of temperature, giving negative temperature coefficients. It was thought that the organic acids would be an interesting class of substances to study as regards their power of forming conducting solutions when dissolved in this medium, and the nature of the variation of the molecular conductivity with dilution, particularly for the more dilute solutions. At the same time it was thought advisable to extend this study to include solutions of these substances in liquid hydrogen chloride, as it has been shown by Steele, McIntosh and Archibald,[3] that in many cases solutions of organic substances in this solvent exceed those formed with the liquid hydrogen bromide in their power of conduction.

It has been pointed out by Walker, McIntosh and Archibald,[4] that several of the organic acids form conducting solutions with liquid hydrogen chloride; but in the case of the hydrogen bromide solutions, the specific conductivity seemed to be so small as to be almost unmeasurable. It will be shown below, that with the form of electrolytic cell here used, the conductivity of a large number of these acids, when dissolved in the liquid hydrogen bromide, can be followed over a considerable range of dilution.

The Materials Used.—The preparation of the liquid hydrogen bromide

[1] This Journal, 29, 665 (1907).

[2] Phil. Trans., A. 205, 99 (1905).

[3] Loc. cit. p. 132.

[4] J. Chem. Soc., 85, 1098 (1904).

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has been already described in the paper referred to above. The hydrogen chloride was generated from sulphuric acid and a saturated solution of sodium chloride. The resulting gas was thoroughly dried by passing through concentrated sulphuric acid, and then through a glass tube 50 cms. long, well packed with anhydrous granular calcium chloride. From here the gas passed directly into the condensing tube, which was immersed in a pasty mixture of solid carbon dioxide and ether. The liquid chloride, dried in this way, had a slightly lower conductivity than that dried by means of phosphorus pentoxide, due, perhaps, to the fact that in the latter case some oxychloride of phosphorus may have been formed, as pointed out by Bailey and Fowler[1] and also by Baxter,[2] and dissolved by the liquid chloride.

The organic acids used were nearly all from Kahlbaum's laboratories, and were in all cases the purest that could be obtained. The purity of the different substances was tested by means of boiling and freezing point measurements.

Apparatus.—The apparatus used in making the following measurements was essentially the same as that used in the case of the alcohol solutions.[3] Two conductivity cells, one for solutions having a high resistance, and the other for use where the resistance was comparatively low, enabled one to follow the conductivity over a considerable range of dilution.

When working with the hydrogen bromide solutions, the conductivity vessel was immersed in the bath of solid carbon dioxide and ether. This bath, if sufficient attention is paid to the stirring, can be kept within at least two tenths of a degree of—80°.

A lower temperature than—80° was necessary when working with solutions in the liquid hydrogen chloride, as this solvent boils at a temperature of—83°. The necessary condition was secured by connecting the vacuum tube containing the carbon dioxide and ether with a good water pump, and in this way keeping a partial vacuum over the cooling mixture. With a steady stream of water passing through the pump, the temperature of the bath remains surprisingly constant for a long time; in the present case at about—96°. So vigorously does the carbon dioxide boil away, that it serves to keep the mixture well stirred. The temperatures were, in all cases, indicated by pentane thermometers, standing in a tube half filled with ether, which in turn passed through the rubber stopper of the vacuum tube well down into the pasty mass of carbon dioxide and ether. These thermometers were made especially for working with these solutions; they were graduated to tenths of a degree, and could easily be read to fiftieths of a degree if necessary.

[1] Chem. News, 58, 22.
[2] This Journal, 28, 770 (1906).
[3] This Journal, 29, 666 (1907).

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The same method of measuring resistance was employed, as was used in the case of the hydrogen bromide solutions of the alcohols—that is, the Kohlrausch method using telephone and alternating current. In the case of the more concentrated solutions, it was found necessary to pay a great deal of attention to the platinizing of the electrodes, if a sharp minimum was to be obtained. Treating the electrodes after the manner suggested by Griffiths, seemed to be an advantage in some cases, but nothing appeared to be more satisfactory than an even and firm coating of the platinum black.

In the case of the more dilute solutions, where the resistance is very high, the conductivity of the solvent has to be subtracted from the conductivity of the solution. For this purpose the conductivity of the solvent must be known as accurately as possible. As I pointed out in a previous communication, it is very difficult to obtain an accurate value for the specific conductivity of these liquid hydrides, the resistance being so high that the minimum point on the bridge cannot be located within several millimeters. The resistance of each particular portion of solvent used was measured as accurately as possible, and the value found was used in calculating the conductivity, in the case of the solutions prepared with this portion of solvent.

The specific conductivity of the liquid hydrogen bromide, as stated in the paper referred to above, was, as an average value, about 0.008×10^{-6} in reciprocal ohms, while the corresponding value for the liquid hydrogen chloride was slightly higher, being 0.010×10^{-6} in the same units.

Although not of vital importance in the present research, it may be asked if this greater conductivity on the part of the liquid hydrogen chloride is due to the presence of impurities, or if it is due to the nature of the hydrogen chloride itself. It will be seen from the results given below, that substances dissolved in this solvent conduct better than when dissolved in the liquid hydrogen bromide. The same amount of impurity present, in the case of the hydrogen chloride, might give a solution which would conduct many times better than the corresponding solution with the liquid hydrogen bromide. As it is practically impossible to prepare any substance absolutely pure, the greater conductivity of the hydrogen chloride might be accounted for in this way. However, it is not very apparent what this impurity can be. As shown by Steele, McIntosh and Archibald,[1] very few of the inorganic salts dissolve in the liquid halogen hydrides, and fewer still give conducting solutions. Among those which do give such solutions, are some phosphorus compounds; but one can hardly imagine phosphorus compounds being present in the liquid chloride prepared after the manner stated above, or in

[1] Loc. cit., p. 122.

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fact any other body, inorganic or organic, which would give a conducting solution. It seems more likely that it is the hydrogen chloride itself which is conducting the electric current, the lower viscosity[1] of the hydrogen chloride accounting, perhaps, for the greater conducting power of this solvent.

In estimating the accuracy with which the molecular conductivity of any given solution could be determined, we should consider first, the error which may be involved in the measurement of the resistance, due to an nnknown change in the temperature of the solution. As we see from the table of temperature coefficients given below, the resistance of some of the solutions may change as much as 3 per cent. for a difference in temperance of 1°. As we pointed out above, the temperature may vary as much as 0.2°. An error therefore of 0.6 per cent. might be made on this account alone. It is not likely that the resistance of any definite solution, provided the temperature remained constant, could be determined within 0.2 per cent, while a still greater error might be made in determining the concentration of the dissolved substance. This error might possibly amount to as much as 0.3 per cent. If now, we assume that these errors all affected the conductivity in the same direction, it is apparent that the measurement of the conductivity might be in error somewhat over 1.0 per cent. ; while in the case of the molecular conductivity, the observed values may be in error as much as 1.5 per cent. For a few of the more dilute solutions, of those substances which give the poorest conducting solutions, the error may be somewhat larger than this ; as there the conductivity of the solvent has been subtracted from that of the solution, and this procedure in itself may lead to an erroneous result ; while an appreciable error in the measurement of the conductivity of the solvent would cause a slight error in the value of the specific conductivity of the dissolved substance.

Qualitative Results.

A large number of the acids were first examined in a qualitative manner only, to ascertain what ones formed conducting solutions with the solvents in question. In preparing the solutions for these measurements, about 20.0 cc. of solvent were used for each determination. The substance, if not a liquid, was always finely powdered before adding it to the solvent. In the case of those substances which either did not dissolve at all or dissolved only in traces, the organic acid was left in contact with the solvent—with frequent stirring—for a long time, in order to allow the solvent to become as nearly saturated with the substance in question as possible. It is worth noting, that in all cases so far met with, solution takes place a great deal more rapidly and equilibrium is

[1] McIntosh and Steele, Loc. cit., p. 118.

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reached much more quickly, than is the case with substances dissolving in water.

In tabulating the results of these experiments, each of the substances examined is considered as belonging to one of three classes, according as it forms a good conducting solution, one which conducts only slightly, or does not give a conducting solution at all. It may be further stated, that the first class would form solutions which have about the same conducting power as that of a fiftieth normal solution of potassium chloride in water; while those in the second group would conduct the current to about the same extent as a sample of ordinary conductivity water.

A blank appearing in the table, indicates that no determination was made to ascertain whether or not that particular acid formed conducting solutions with the solvent in question.

While no absolute measurements were made to determine whether or not a certain substance was soluble in either solvent, almost certain indications could be obtained as to its solubility or non-solubility, by adding, at first, a very small portion of the substance in question to the pure solvent, leaving it for some time—with repeated stirring—and noting whether or not it had dissolved. The amount of heat given out, too, when the organic acid is added to the liquid hydride, serves as a very good indication of whether or not the acid has dissolved; as in all cases where solution is known to take place, there is a marked evolution of heat. It should be stated here, that I have not met with any case where solution of an organic substance is known to have taken place without causing a marked increase in the conductivity above that of the pure solvent.

It will be noticed at once, that, in general, the acids of the paraffin series form conducting solutions with both solvents; the exceptions being, formic acid in the case of hydrogen bromide, and the higher members of the series with both solvents. It is apparent, too, that the conductivity falls off as we approach the higher members of the series; caprylic acid forming solutions which conduct only slightly, while palmitic acid does not conduct at all in hydrogen bromide. The behavior of formic acid is rather anomalous, as, judging from the rest of the series, we would expect it to be the best conductor of them all. However, it is a rather poor conductor when dissolved in hydrogen chloride, while it will apparently not dissolve in hydrogen bromide, and certainly does not conduct at all.

The dibasic acids, belonging to the oxalic acid group, do not conduct with either solvent; indeed, these acids did not appear to dissolve at all in the liquid hydrides. The dibasic acids of the ethylene group, while not forming conducting solutions with hydrogen bromide, have fair conducting power when dissolved in hydrogen chloride. In fact, at the con-

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TABLE I.—QUALITATIVE RESULTS.

Name of organic acid	Conducting power of solution formed with the halogen hydrides: Hydrogen bromide	Hydrogen chloride
Formic acid	no conduction	good
Acetic acid	good	good
Propionic acid	good	good
Butyric acid	good	good
Isovaleric acid	good	
Caprylic acid		slight
Palmitic acid	no conduction	
Oxalic acid		no conduction
Malonic acid	no conduction	no conduction
Sebacic acid	no conduction	no conduction
Glycollic acid		no conduction
Lactic acid	no conduction	
Malic acid	no conduction	no conduction
Tartaric acid	no conduction	no conduction
Racemic acid	no conduction	no conduction
Citric acid	no conduction	no conduction
Saccharic acid		no conduction
Amino-succinamic acid		no conduction
Fumaric acid	no conduction	slight
Maleic acid		good
Mesaconic acid		no conduction
Sorbic acid		slight
Benzoic acid	good	good
Ortho-nitro benzoic acid	no conduction	
Meta-nitro benzoic acid	slight	slight
Para-nitro benzoic acid	no conduction	
Ortho-amino benzoic acid	no conduction	
Hippuric acid	no conduction	slight
Ortho-toluic acid	good	good
Meta-toluic acid	good	good
Para-toluic acid	good	good
Ortho-phthalic acid	no conduction	good
Meta-phthalic acid	no conduction	no conduction
Ortho-hydroxy benzoic acid	good	good
Para-hydroxy benzoic acid	no conduction	slight
Tannic acid	no conduction	
Cinnamic acid	slight	good
Cumaric acid	no conduction	

centration examined, maleic acid had as good conducting power as any other acid examined at this particular concentration.

It is worth noting that the monobasic acids, carrying an hydroxyl group, as in the case of lactic and glycollic acids, do not form conducting solutions with the halogen hydrides.

In the case of the acids of the benzene series, conducting solutions seem to be formed with both solvents, as shown in the cases of benzoic

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and the toluic acids. The behavior of the hydroxy benzoic acids seems to vary with the position of the hydroxyl radical. When this radical is ortho to the carboxyl group (salicylic acid) we have good conducting solutions formed with both solvents, while the para acid conducts slightly when dissolved in hydrogen chloride, but not at all when treated with the liquid hydrogen bromide. The same is true of the phthalic acids: *o*-phthalic acid gives good conducting solutions with hydrogen chloride, while the meta acid does not apparently dissolve at all. The same behavior is noticed in the case of the oxybenzoic acids when dissolved in water, for there the conductivity of the ortho acid is many times greater than that of the meta. while the meta acid in turn, is a much better conductor than the para.

It will be remembered, that, in the case of the hydrogen bromide solutions of the alcohols, it was generally true, that when the hydroxyl radical was in the meta position the alcohol gave a better conducting solution than when this radical had any other position. In the case of the present solutions, it would seem to be the ortho acid which forms the best conducting solutions. At least this is what one would conclude from the qualitative results, as shown for instance in the case of the phthalic and hydroxy benzoic acids.

The mono and dihydroxy dibasic acids do not form conducting solutions with either solvent.

Solutions of the nitro benzoic acids show only slight conducting power, while ortho-amino-benzoic acid does not form conducting solutions, at least not with hydrogen bromide.

It appears, then, that the action of these solvents is somewhat selective, as in the case of formic, salicylic and ortho-phthalic acids. It seems safe to say, however, that more of the organic acids will form conducting solutions with hydrogen chloride than with hydrogen bromide. Is this due to the lower temperature, or to the nature of the hydrogen chloride itself?

It has been shown by Archibald and McIntosh[1], that, in all cases where organic bodies dissolve in the liquid hydrides to give conducting solutions, there is present some element which may increase in its power of combining with others. Thus, in the case of the ethers, aldehydes and alcohols, it has been shown that when these substances dissolve in the liquid hydrides, compounds are formed between the hydrides and the organic substances, in which the oxygen probably functions as a quadrivalent element. It would seem from the above measurements, however, that the presence of oxygen atoms in the molecule is not a sufficient reason for supposing that the substance will dissolve or form conducting solutions with these solvents. Thus, if we examine the above table, we see, that, in general, the greater number of carboxyl groups or of hy-

[1] Pr. Roy. Soc. Canada, [2], III, 10, 43 (1904).

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droxyl radicals present in the molecule, the less likely is the substance to dissolve. Thus we may instance citric acid, a mono hydroxy tribasic acid; and tartaric and racemic acids, dihydroxy dibasic acids; also the dibasic acids of the oxalic acid group. On the other hand, the monobasic acids of both the paraffin and benzene series form good conducting solutions.

This behavior, on the part of those acids which contain a larger number of oxygen atoms in the molecule, might at first seem to be opposed to the idea that the valence of the oxygen has increased at the lower temperature here obtaining. But, if we look further into the matter, it seems to me that the fact that these acids do not form conducting solutions, rather supports this idea than otherwise.

If we consider an hydroxy polybasic acid, when the temperature of such a subtance is lowered, while this may be attended with an increase in the valence of the oxygen, there is here some likelihood that the free valences of one oxygen may be satisfied by the free bonds of another, there being a great many ways in which such a combination can take place. While, in the case of a monobasic acid, the number of ways in which such a neutralization may occur is greatly reduced. The valence then of the oxygen belonging to the polybasic acid may increase, but it does not necessarily follow that the substance will dissolve in the liquid hydride, to give addition compounds which undergo ionic dissociations.

Quantitative Measurements.

Results with Hydrogen Bromide. The results of the quantitative measurements carried out with solutions in liquid hydrogen bromide, are set forth in Table 2. Under the heading, dilutions, are given the number of liters which contain a gram of molecule of the dissolved substance. While the molecular conductivites—expressed in reciprocal ohms—will be found in the remaining columns. The values here given were obtained from the dilution—molecular conductivity curves, shown below, where the original measurements, by aid of which these curves were drawn, are indicated, at least over the greater part of the dilution examined.

In Table 3 are shown the temperature coefficients of the conductivity for the hydrogen bromide solutions, expressed as percentage values of the conductivity at —80°. The first column of the table shows the dilutions of the particular solutions examined.

It has been already noted that formic acid does not form a conducting solution with hydrogen bromide. The other members of this series, however, which have lower molecular weights than that of caprylic acid, do form conducting solutions with this solvent. And here, as in the case of the corresponding alcohol solution, the conductivity, particularly

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TABLE 2.

HYDROGEN BROMIDE SOLUTIONS—VALUES OF THE MOLECULAR CONDUCTIVITIES.

Dilutions	Acetic Acid	Butyric Acid	Isovaleric Acid	Benzoic Acid	o-Toluic Acid	m-Toluic Acid	p-Toluic Acid	Salicylic Acid
250.0								80.0
200.0								76.2
125.0								72.0
100.0								70.0
50.0								71.0
40.0				2.794	6.31			76.1
20.0			8.04	4.12	8.12	3.95	6.12	100.5
12.50	5.68		9.22	5.80	10.23	5.79	8.16	141.3
10.00	6.80	5.80	10.12	7.15	12.56	7.27	10.26	168.2
6.66	11.21	10.35	13.75	13.12	18.85	16.61	19.62	233.8
5.00	18.4	15.10	19.90	19.75	29.71	21.81	30.4	294.5
4.00	29.8	23.9	28.2	31.7	39.3	32.1	46.1	354.
3.33	44.8	34.3	39.3	44.2	49.9	48.3	63.5	407.
2.857	62.5	46.2	52.4	58.8	63.8	64.1	82.0	452.
2.500	81.4	61.7	68.2	77.9	81.3	84.5	104.7	490.
2.222	103.0	79.3	88.1	100.9	99.7	107.1	129.5	523.
2.000	123.5	98.5	107.7	127.8	120.0	132.8	155.0	552.
1.666	171.0	143.3	146.8	187.9	164.0	186.1	210.4	604.
1.428	215.0	188.0	183.3		205.6	238.2	262.6	650.
1.250	252.0	225.4	212.0		226.0	294.1	324.4	
1.000	332.0	277.4	254.7		150.0	435.		
0.833	408.	314.1	285.2					
0.714	465.	339.0	307.5					
0.666	491.							
0.625	511.							
0.588	518.							
0.555	524.							

for the more concentrated solutions, is the greater the lower the acid comes in the series. The opposite seems to be true for the acids of the benzene series, for here benzoic acid does not conduct as well as ortho and para toluic acids. And this again is parallel with the case of the alcohols, where thymol gave better conducting solutions than the lower cresols, and these in turn were better conductors than phenol.

If we examine the values of the molecular conductivities of the more dilute solutions of these acids, it will be seen that only in the case of salicylic acid is there any indication of an increase in the molecular conductivity with dilution. For all the other acids examined, there is a continual rise in the molecular conductivity as the solution becomes more concentrated. In some cases it increases nearly one hundred times, in passing from a tenth normal to a normal solution. It will be remembered that in the case of the dilute solutions of some of the alcohols in hydrogen bromide, the molecular conductivity was found to increase with the dilution. It should be noted in passing, that it is the acid which has the highest conducting power, that shows this interesting variation.

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TABLE 3.

HYDROGEN BROMIDE SOLUTIONS—TEMPERATURE COEFFICIENTS OF CONDUCTIVITY

Dilutions	Temp. limits	Acetic Acid	Butyric Acid	Isovaleric Acid	Benzoic Acid	*o*-Toluic Acid	*m*-Toluic Acid	*p*-Toluic Acid	*o*-Hydroxy benzoic Acid
18.42	—80° and —76°								1.00%
8.82	—80° and —75°				0.53%				
6.65	—80° and —75°							At this dilu-	
5.85	—80° and —76°						0.15%	tion there is	
5.26	—80° and —74°					At this dilu-		no percepti-	
4.37	—80° and —75°			2.45%		tion there is		ble change in	
4.30	—80° and —73°	2.62%				no percepti-		conductivity	
4.18	—80° and —75°		2.68%			ble change in		between	
2.38	—80° and —75°				0.72%	conductivity		these tem-	
1.83	—80° and —76°					between	0.93%	peratures	
1.36	—80° and —76°					these tem-			2.15%
1.136	—80° and —75°				0.89%	peratures			
0.817	—80° and —73°		3.70%						
0.729	—80° and —75°			3.96%					
0.571	—80° and 73°	2.72%							

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The temperature coefficients seem to vary in a regular manner, increasing slightly with the concentration of the solution. It is noteworthy that the magnitude of this quantity should be so different for the different acids. In some instances it is larger than for water solutions of the inorganic electrolytes, while in other cases it has practically disappeared; the temperature having apparently no effect on the conductivity within the narrow range here examined. As opposed to the above water solutions, where the temperature coefficient of conductivity almost invariably increases with the dilution, we see that here the variation is in the opposite direction. This would seem to be further evidence to show that we are here dealing with a much more complex electrolyte than in the case of the water solutions.

A change in the conductivity of a solution, following a change in the temperature, may be due, either to a change in the degree of the ionization of the electrolyte, a change in the viscosity of the solution, or a change in the mobility of the ions, to any one, or to all of these combined. Now the change in the viscosity of the solutions, within the range of temperature here considered, must be practically the same for all these solutions. However, it is conceivable that the change in the speed of the ions, due to this change in viscosity, might be very different in the case of an ion of which acetic formed a part, from what it is in the case of a toluic acid ion. But it is the acetic acid which has the larger temperature coefficient of conductivity; while if the change in viscosity has much influence in changing the conductivity, we would expect the more complex ion to be effected the more. It would seem then, that the change in conductivity, caused by the change in temperature, must be due chiefly to a change in the degree of ionization of the electrolyte.

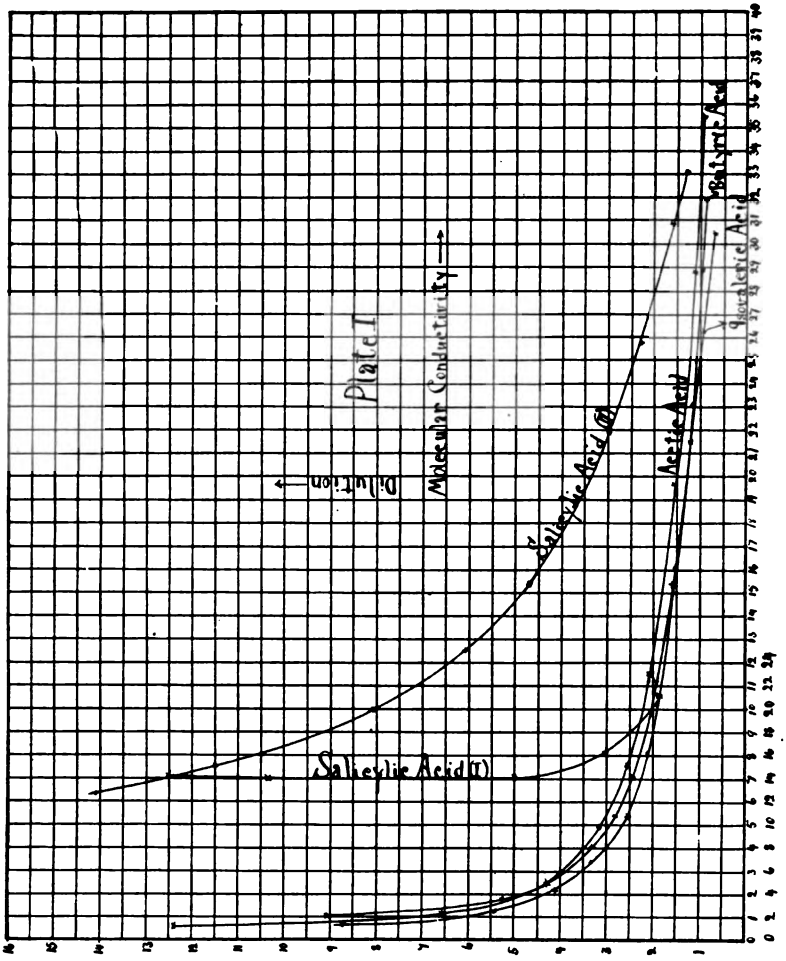
In working with hydrogen bromide solutions of the alcohols, a number of cases were found where the solutions had negative temperature coefficients. No such cases were met with in the work with the organic acids, although in some instances the coefficient was exceedingly small.

The relation between the dilution and the molecular conductivity is shown graphically in Plates I and II, where the ordinates represent the dilutions and the abscissae the molecular conductivities. The values here indicated are the experimental ones, and those previously given, for the round numbers, were obtained from such curves as these, except that they were plotted on a larger scale.

The relative conducting power of the several acids is here clearly shown, particularly for the more concentrated solutions. Attention should be called to the curves for isovaleric and acetic acids. These are seen to cross each other at a dilution of about 4.5 liters the isovaleric acid solutions being better conductors than those of acetic acid, in the more dilute solutions while in the case of the more concentrated solutions,

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the acetic acid is the better conductor. This is parallel to the behavior of acetic and butyric acids in water solutions, as we will show further on,

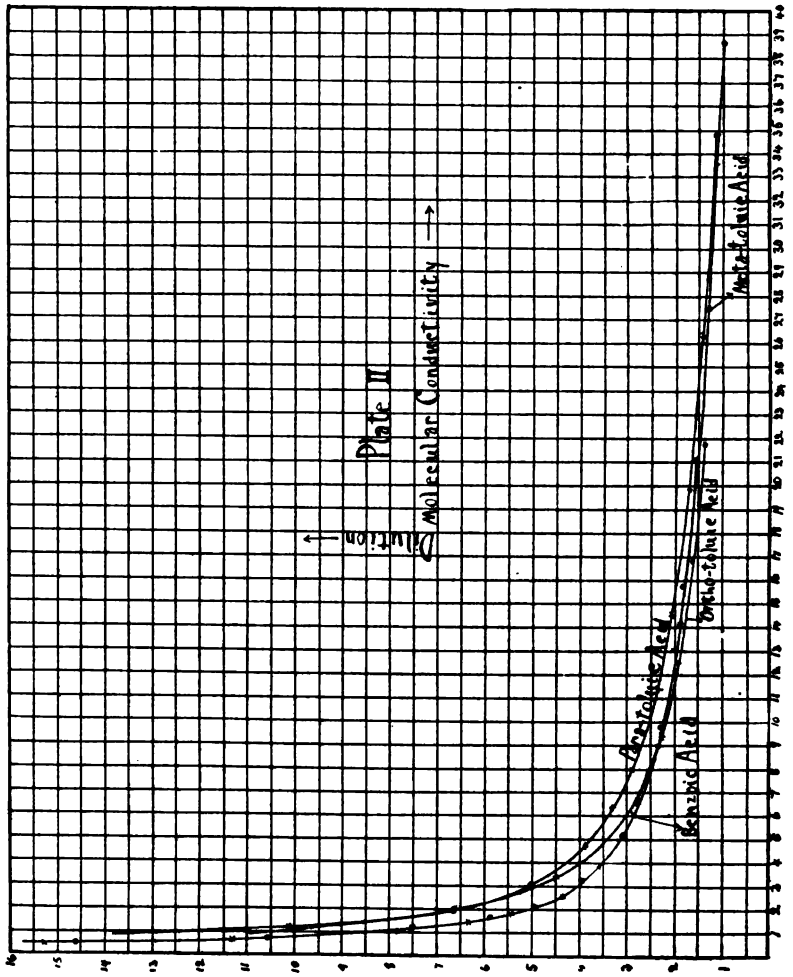


the butyric acid being the better conductor in the dilute solutions, but the acetic acid being the better in the more concentrated.

As the different curves, with the exception of the first part of the salicylic acid curve, are all plotted to the same scale, it will be seen that the acids of the acetic acid group, have almost the same conducting power as those of the benzoic acid group. It is also noticeable that salicylic acid exceeds all the others in conducting power.

Results with Hydrogen Chloride.— The quantitative results for solutions in the liquid hydrogen chloride are given in Table 4. The different values are expressed in terms of the same units as employed in the

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previous table; the values for the molecular conductivity being taken from the dilution—molecular conductivity curves shown below.

The temperature coefficients of conductivity, for the hydrogen chloride solutions, expressed in terms of the same units as the corresponding values for the hydrogen bromide solutions, are given in Table 5. The dilutions to which these measurements refer are also included in the table.

The temperature coefficients can be dismissed with a few words. Here, as in the case of the hydrogen bromide solutions of these substances, they seem to vary in a regular manner, and are all positive, although some are very small. It is noticeable that benzoic and toluic acids have much larger temperature coefficients here than in the case of the hydrogen

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bromide solutions. It will be seen, too, that the coefficient increases from the formic acid up to butyric acid.

TABLE 4.

HYDROGEN CHLORIDE SOLUTIONS—VALUES OF THE MOLECULAR CONDUCTIVITIES.

Dilutions	Formic acid	Acetic acid	Propionic acid	Butyric acid	Benzoic acid	*m*-Toluic acid	*o*-Phthalic acid	*o*-Hydroxybenzoic (Salicylic) acid	*p*-Hydroxybenzoic acid
1000.							2278.	1687.	
800.							2250.	1533.	
666.							2204.	1438.	
500.							2094.	1314.	
333.					49.8		1688.	1176.	
250.0					51.1		1466.	1112.	
200.0			248.6		51.8			1065.	
142.8			235.5		54.2			1004.	
125.0			226.1	160.0	56.0	72.1		976.	
100.0		243.3	215.2	156.2	58.2	75.0		964.	
66.6	33.2	231.3	193.5	147.0	63.6	83.2		861.	4.45
50.0	33.6	222.7	185.0	142.0	70.0	88.4		775.	4.02
40.0	34.2	217.5	179.3	138.3	76.1	94.6		720.	3.70
25.0	35.7	211.5	180.0	135.0	94.0	114.8		874.	3.07
20.0	37.6	208.6	180.8	134.3	105.8	128.6		921.	
14.28	41.8	210.8	182.6	136.6	129.7	158.0		988.	
12.50	43.8	216.1	192.3	138.8	139.6	177.0		1023.	
10.00	47.2	236.4	214.2	146.3	162.0	207.5		1074.	
6.66	53.4	315.6	275.6	168.0	240.0	311.8		1167.	
5.00		387.5	331.	205.0	230.0	447.5		1250.	
4.00	66.7	454.	381.	246.2		588.		1298.	
3.33	93.2	525.	485.	285.0		699.		1314.	
2.50	127.8	657.	622.	359.				1280.	
2.00	165.0	769.		433.				1269.	
1.428	267.1	948.		562.					
1.000	436.	1112.		730.					
.666	712.								
.500	921.								

TABLE 5.

HYDROGEN CHLORIDE SOLUTIONS—TEMPERATURE COEFFICIENTS OF CONDUCTIVITY.

Dilutions	Temp. limits	Formic acids	Acetic acid	Propionic acid	Butyric acid	Benzoic acid	*m*-Toluic acid	*o*-Phthalic acid	*o*-Hydroxybenzoic acid
190.5	—92° and —87°							0.20%	
50.0	—93° and —87°				2.80%				
36.02	—91° and —88°								1.15%
16.13	—92° and —87°						1.40%		
11.81	—92° and —88°			2.15%					
5.00	—92° and —88°		1.92%						
4.42	—92° and —88°					1.65%			
2.50	—92° and —88°			2.91%					
.792	—93° and —87°				3.27%				
.479	—92° and —88°	1.15%							

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It is noteworthy that in this solvent the conductivity of the paraffin series of acids, for all dilutions, increases from the higher members of the series down, until we reach formic acid, which is much below acetic acid in its conducting power. It will be recalled that this substance did not conduct at all, or apparently dissolve in the liquid hydrogen bromide. In the hydrogen chloride it has about the same conducting power as acetic acid in hydrogen bromide. It is apparent, too, that there is a much greater difference in conductivity between the acids in this series, in the present instance, than was the case with the hydrogen bromide solutions.

It will further be seen, that here the acids of the paraffin series are much better conductors than those of the benzene series, while, in the case of the hydrogen bromide solutions, they were about equal in conducting power. It will be noticed, too, that salicylic and phthalic acid solutions surpass all the other solutions of equal concentration, in their power of conducting the current; the molecular conductivity, in the case of these two acids, having about eight times as great a value as it has in any other case.

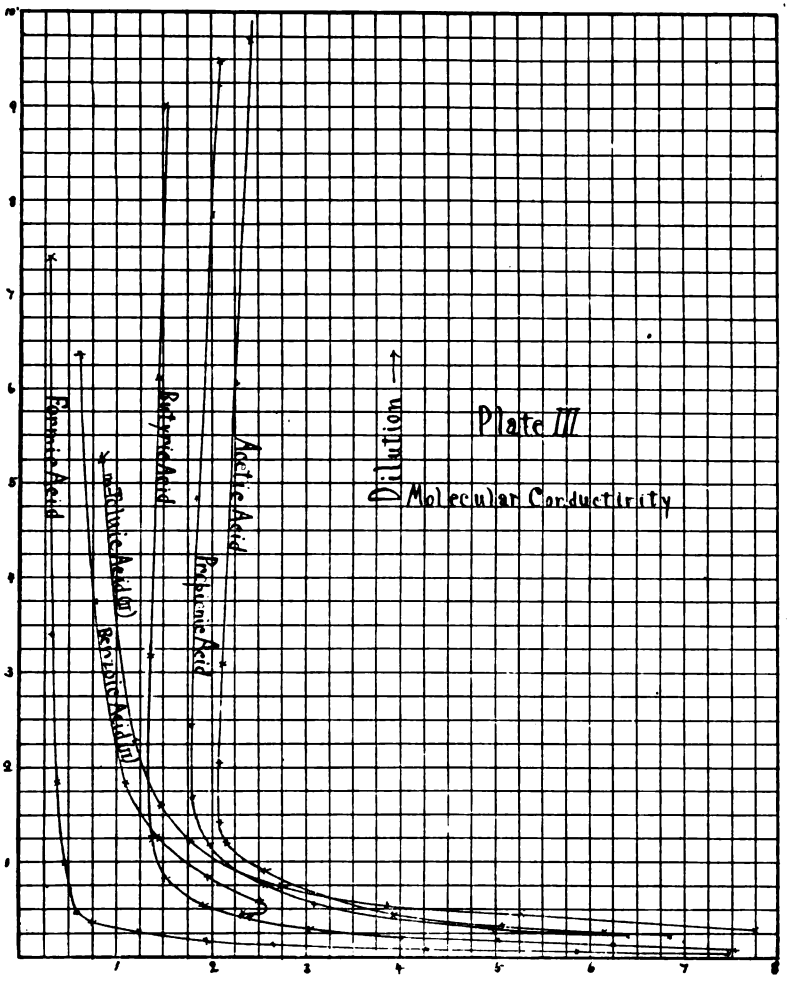
If we examine the variation of the molecular conductivity with the dilution, for these hydrogen chloride solutions, we notice at once, that, for the dilute solutions, if we except the three acids, formic, *p*-toluic and benzoic, the molecular conductivity always increases as the dilution increases. This interesting variation, which is the same as we have in the case of water solutions of the ordinary electrolytes, is much more marked than in the case of the hydrogen bromide solutions of the alcohols. However, after a certain concentration is reached which is very much the same for all the acids, the molecular conductivity begins to increase with decreasing dilution; a variation which we have found for solutions of most of the organic substances in the liquid hydrides.

If we compare the values for the molecular conductivity, obtained with the hydrogen bromide solutions, with those given above for the hydrogen chloride, we see that the solutions in the latter solvent conduct much better than those in the former. Phthalic acid, which would not conduct in hydrogen bromide, gives solutions of high conductivity with hydrogen chloride. This difference is much greater for the dilute solutions than for the more concentrated. In fact, the molecular conductivity for hydrogen chloride solutions of acetic acid, at a dilution of 10.0 liters, is about forty times as great as for the corresponding hydrogen bromide solutions, while, at a dilution of 1.0 liters, it is only about three times as large.

The variation of molecular conductivity with dilution, for the hydrogen chloride solutions, is shown graphically in Plates III and IV; where the dilutions as ordinates are plotted against the molecular conductivities as abscissae. Here the curve for butyric acid is seen to be behind that

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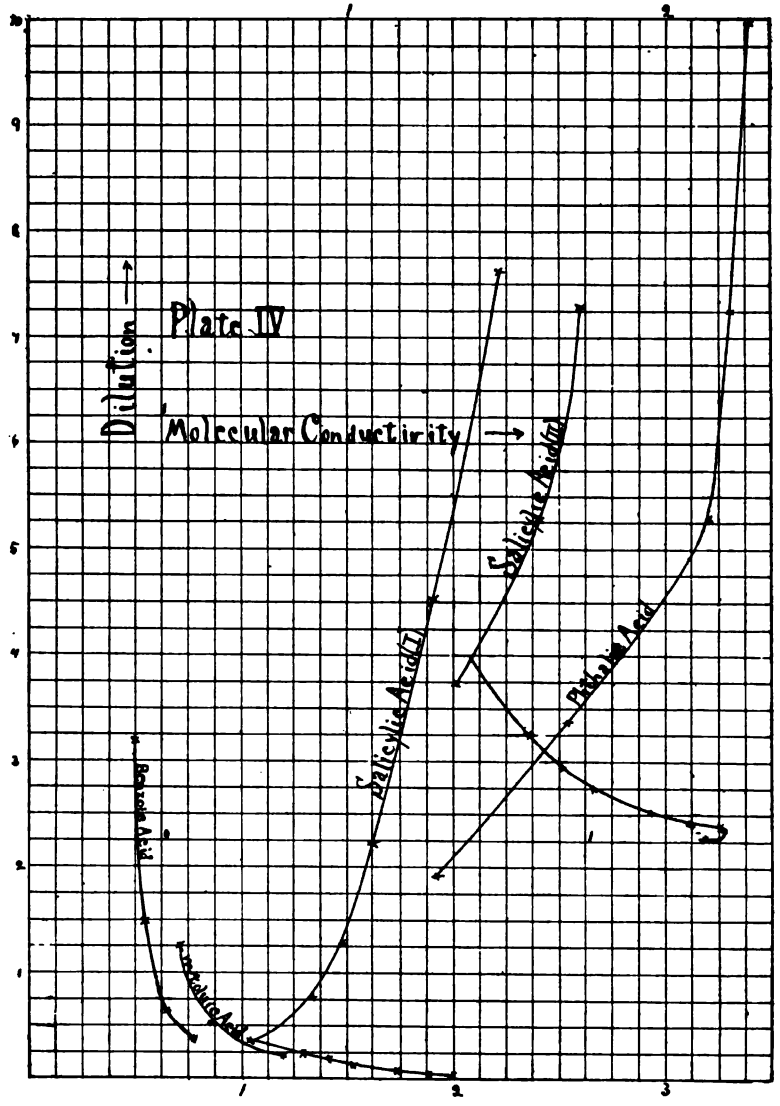
for propionic, throughout its entire length. The same may be said of the propionic acid curve as compared with the acetic; the formic acid curve, however, lies far behind the others.



The increase of the molecular conductivity with dilution for the more dilute solutions, is here shown by the slope of the first part of the curve backward, toward the y-axis. This is exaggerated in the case of salicylic acid, until we have here apparently two curves meeting at a dilution of about 380.0 liters. There is here probably some radical change in the addition body which forms, and which undergoes ionic dissociation. It should be stated that no change could be noticed in the solution at this point; it appeared perfectly homogeneous.

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From an examination of the curves for the hydrogen chloride solutions, it appears that the variation of molecular conductivity with dilution changes its character at almost the same dilution in each case. It seems



probable that in the case of these acids, in the dilute solutions, and up to a certain concentration, the addition substance which is formed between the organic acid and the hydrogen chloride, and which subsequently undergoes ionic dissociation, has a very simple structure; perhaps one molecule of the hydrogen chloride uniting with one molecule of the or-

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ganic acid. In such a case the molecular conductivity would be given by the expression κV where κ is the specific conductivity, and V the dilution; and here the molecular conductivity, as given by this expression, should increase with the dilution. On the other hand, in the more concentrated solutions, it is not unlikely that we have a much more complex addition compound formed, and, supposing it contained n-molecules of the dissolved substance, the concentration of the compound will be proportional to the nth power of the concentration of the dissolved substance, and the molecular conductivity, as pointed out by Steele, McIntosh and Archibald[1], will be given by the expression κV^n, rather than by κV. The molecular conductivity as calculated from the expression κV, will, in such a case, decrease with the dilution. And this is what we find to be the case for these acids, in their more concentrated solutions.

Attention should also be drawn to the fact, that the increase of molecular conductivity with dilution, is more marked in the case of those acids which give the best conducting solutions, for instance, the solutions of salicylic, phthalic and acetic acids. This is surely in line with the argument we have used above, for, the conductivity of a solution will depend largely upon the number of ions there are present in a given volume, and this will be the greater, other things being equal, for a given concentration of the dissolved substance, the less the number of molecules of the organic acid there are used up to form one molecule of the electrolyte. In a dilute solution, under these conditions, if you assume one molecule of solute to be associated with one of solvent to give the electrolyte, as more of the solute is added, the molecular conductivity will decrease owing to a decrease in the degree of ionization. As the solution becomes more concentrated, however, and the character of the electrolyte changes, becoming more complex in composition, the effect on the molecular conductivity due to the decrease in ionization, will be overshadowed by the effect due to the change in the concentration of the electrolytic compound which will now be proportional to the nth power of the concentration of the dissolved substance.

Some reference should be made to the curve for phthalic acid. Here the measurements extend over only a short range of dilution. Apparently the acid was only slighty soluble in the liquid hydrogen chloride, as, at a dilution of about 250.0 liters, the specific conductivity became constant, and the addition of more substance produced no change in the conductivity, and apparently did not go into solution at all.

It is noteworthy, too, that in this case the molecular conductivity continues to increase with the dilution over the whole range investigated.

Those parts of the curves for benzoic and salicylic acids, which correspond to their more concentrated solutions, are seen to turn back and

[1] Loc. cit., p. 152.

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downward, showing that the molecular conductivity of their solutions is decreasing with the concentration, although the specific conductivity was still increasing as more substance was added to the solution. This behavior was noticed, too, in the case of hydrogen bromide solutions of methyl alcohol. Either the acid which is dissolved by the solution is only in part used to form more of the electrolytic compound, or of that which is formed, only a small portion is subsequently ionized.

It is interesting to compare the values of the molecular conductivity for some of these organic acids, when dissolved in the liquid hydrogen chloride, or hydrogen bromide, with the corresponding values obtained for solutions in water. Table 6 contains such data for solutions of acetic, butyric and benzoic acids, in the several solvents, as well as for solutions of ethyl alcohol and thymol in hydrogen bromide.

It will be noted, that, for the dilutions which are common to all, the three acids conduct better when dissolved in the liquid hydrides than when dissolved in water. It is almost certain, however, that at greater dilutions than could be examined for the hydrogen bromide solutions, the molecular conductivity of the aqueous solutions of these acids would be greater than those for the hydrogen bromide solutions.

It will be seen, too, from this table, that the hydrogen bromide solutions of ethyl alcohol are much behind, while those of thymol far surpass

TABLE 6.

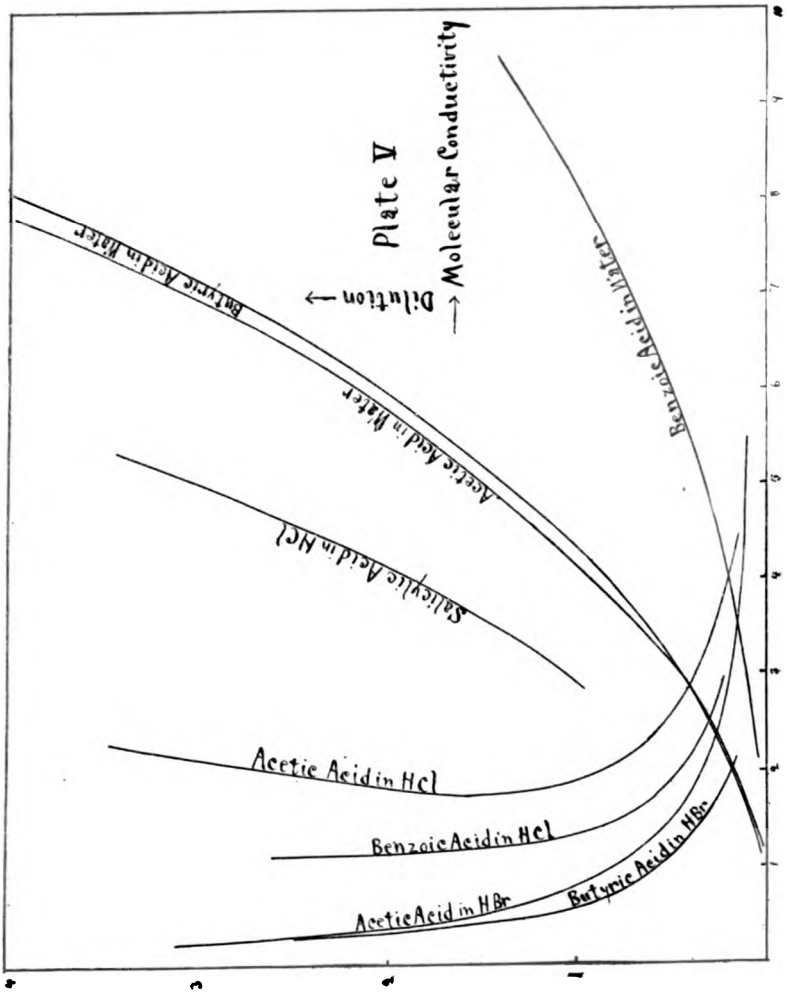
MOLECULAR CONDUCTIVITY VALUES FOR VARIOUS SOLVENTS.

	Aqueous Solutions			Hydrogen Bromide Solutions					Hydrogen Chloride Solutions		
Dilutions	Acetic Acid	Butyric Acid	Benzoic Acid	Acetic Acid	Butyric Acid	Benzoic Acid	Ethyl Alcohol	Thymol	Acetic Acid	Butyric Acid	Benzoic Acid
2500.	64.8	66.5	...	...	...	...		...			
2000.	58.0	59.8	...	...	...	...		...			
1500.	50.2	52.0	...	..	...	...		...			
1250.	46.2	48.1	90.0	...	...	...		...			
1000.	41.5	43.4	81.5	...	...	...		...			
750.	36.8	38.2	71.8	...	..	...		...			
500.	31.2	31.4	60.0	...	...	...		56.9			
250.	22.7	22.5	44.5	...	...	...		...			51.1
125.	18.0	17.1	31.9	...	...	...		76.4		160.6	56.0
100.	...	...	...	...	...	...		88.5	243.3	156.2	58.2
50.0	...	...	...	...	...	...		132.5	222.7	142.0	70.0
40.0	9.2	8.9	...	...	...	2.794		164.8	217.5	138.3	76.1
25.0	...	...	...	...	...			278.6	211.5	135.0	94.0
20.0	7.3	7.0	...	...	...	4.12		394.4	208.6	134.3	105.8
12.50	5.3	4.9	...	5.68	...	5.80	0.486	717.	216.1	138.8	139.6
10.00	4.8	4.5	...	6.80	5.80	7.15	0.485	974.	236.4	146.3	162.0
5.00	3.4	3.0	...	18.4	15.1	19.75	0.502		387.5	205.0	230.0
4.00	3.1	2.7	...	29.8	23.9	31.7			454.	246.2	
3.33	...	...	...	44.8	34.3	44.2	0.605		525.	285.0	
2.00	2.12	1.8	...	123.5	98.5	127.8	1.002		769.	433.	

the corresponding solutions of the acids, in conducting power.

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The form of the dilution—molecular conductivity curve, for solutions of these acids in the several solvents, are shown in Plate V, where the



ordinates represent the dilutions, and the abscissae the molecular conductivities. The curves for the halogen hydride solutions all differ in form from those for the water solutions, with the exception of salicylic acid for its more dilute solutions, that being the only part represented here. It seems likely, however, that if the acetic acid curve could be drawn for much more dilute solutions, that it, too, would have the shape of the water solution curves at its upper extremity.

Attention was drawn above to the fact that, for the more dilute solutions of isovaleric and of acetic acid in hydrogen bromide, the former

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acid exceeded the latter in conductivity, while in the more concentrated solutions the acetic acid is the better conductor. The same variations for the water solutions of acetic and butyric acids is shown here by the curves crossing at a dilution of about 350.0 liters; the butyric acid being the better conductor in the dilute and the acetic the better in the concentrated solutions.

As pointed out above, Steele, McIntosh and Archibald have shown, that, where a substance dissolves and combines with the solvent to give an addition compound which contains n molecules of the dissolved substance, and which subsequently undergoes ionic dissociation, the concentration of the electrolytic compound would be proportional to the nth power of the concentration of the dissolved substance, and the molecular conductivity would be given by the expression κV^n. McIntosh[1] has shown that such addition compounds of the organic acids and the halogen hydrides may be prepared. For instance, in the case of acetic acid and hydrogen chloride, the compound which separates out has the composition $(CH_3COOH)_2$-$(HCl)_3$. In the case of acetic acid and hydrogen bromide, Tschitschibabin[2] obtains a compound $(CH_3COOH)_2HBr$. If then, we calculate the molecular conductivity from the expression κV^n, we may expect to obtain a series of values which vary with dilution as the molecular conductivity varies in the case of water solutions.

Such values have been calculated in a few instances for solutions in both the halogen hydrides, where there was a marked decrease in the molecular conductivity with dilution, and the results obtained are shown in Table 7, together with the dilutions to which these values apply.

TABLE 7.

VALUES OF κV^n

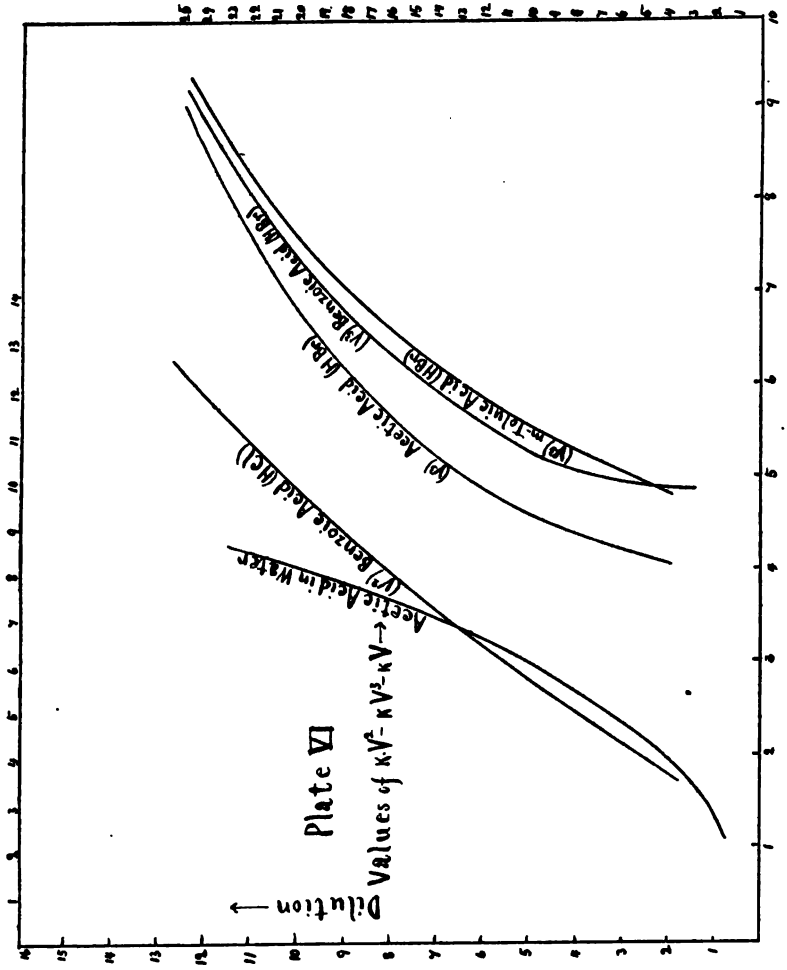
Dilutions	Hydrogen Bromide Solutions						Hydrogen Chloride Solutions	
	Acetic Acid		Benzoic Acid		*m*-Toluic Acid		Benzoic Acid	*m*-Toluic Acid
	κV^2	κV^3	κV^2	κV^3	κV^2	κV^3	κV^2	κV^2
250.0							12.78	9.01
200.0							10.36	7.50
125.0							7.00	4.42
100.0							5.82	3.78
50.0							3.50	2.87
40.0							3.04	2.57
25.0							2.35	2.21
20.0							2.11	2.07
12.50	0.071	0.88	0.073	0.91	0.073	0.91	1.74	
10.00	0.068	0.68	0.072	0.72	0.073	0.73	1.62	
6.66	0.075	0.50	0.087	0.58	0.111	0.74		
5.00	0.092	0.46	0.099	0.49	0.109	0.55		
4.00	0.119	0.48	0.126	0.51	0.128	0.51		
3.33	0.149	0.50	0.147	0.49	0.161	0.54		
2.50	0.204	0.51	0.195	0.49	0.211	0.53		
2.00	0.247	0.49	0.256	0.51	0.266	0.53		
1.25	0.32	0.39			0.367	0.46		
1.00	0.33	0.33			0.435	0.44		

[1] This Journal, 28, 588 (1906).

[2] J. Russ. Phys. Chem. Soc., 7, 1058 (1906).

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It will be seen that by making $n = 2$ in the case of the hydrogen chloride solutions, and $n = 3$ for the hydrogen bromide solutions, we obtain a series of values which increase as the dilution increases. However, if we represent these results graphically, as we have done in plate VI,



plotting the dilutions as ordinates and the values of κV^n as abscissae, we obtain a different form of curve from that for water solutions.

It is obvious that it would be of considerable interest to determine to what extent these organic substances, as well as some inorganic ones, form conducting solutions with liquid hydrogen fluoride. Experiments with this end in view are being started, and it is hoped, that before long, some results worth communicating may be obtained.

The work described in the preceding pages shows :

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(1) That in the case of the monobasic organic acids, the members of the benzene series, and the lower members of the paraffin series, dissolve in the liquid hydrogen chloride and bromide to give conducting solutions; the only exception to this being formic acid, which does not give conducting solutions with hydrogen bromide.

(2) That the polybasic acids do not, in general, give conducting solutions with either solvent, the exceptions here being the dibasic acids of the ethylene group, racemic and fumaric, which give conducting solutions with hydrogen chloride. The fact that the polybasic acids did not give conducting solutions with the halogen hydrides was explained, by assuming that the free bonds of one oxygen atom were satisfied by the free bonds of another, there being here a great many ways in which such a combination could take place.

(3) That for the hydrogen bromide solutions, the molecular conductivity decreases rapidly with increasing dilution; the one exception being salicylic acid, which in the case of a few of the more dilute solutions, shows an increase in the molecular conductivity with dilution.

(4) That, in the case of the greater number of the hydrogen chloride solutions, the molecular conductivities for the more dilute solutions increases with the conductivity, this increase being the more marked the higher the conductivity of the acid. For all the concentrated solutions, however, the molecular conductivity increases rapidly as the dilution decreases.

(5) That for the hydrogen chloride solutions of the paraffin series of monobasic acids, the conductivity increases from butyric acid down, until we reach formic acid, which has a much lower conductivity than the acids which stand next above it in the series.

(6) That the temperature coefficients of conductivity are in all cases positive, although they vary greatly in magnitude on passing from one acid to another. It was shown, too, that the more concentrated the solution the larger the temperature coefficient.

(7) That in the case of acetic, butyric and benzoic acids, the halogen hydride solutions have a higher conductivity than the water solutions, at least for those dilutions for which we have measurements in common.

(8) That, if we take cases where the molecular conductivities, as calculated from the expression κV, decrease with dilution, and calculate them anew from the expression, κV^n, where n is the number of molecules of dissolved substance associated with the solvent to form the electrolyte, we obtain a series of values which vary in the same manner as the molecular conductivities for water solutions of inorganic electrolytes.

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In conclusion, I wish to record my appreciation of a grant from the trustees of the Elizabeth Thompson Science Research Fund, which helped to defray the expenses incurred in carrying on this work.

CHEMICAL LABORATORY,
SYRACUSE UNIVERSITY,
Syracuse, N. Y.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY. NO. 142].

MOLTEN HYDRATED SALTS AS SOLVENTS FOR THE FREEZING POINT METHOD II.

BY J. LIVINGSTON R. MORGAN AND F. T. OWEN.

In a recent paper[1] Morgan and Benson have shown that the molten hydrated salts $CaCl_2.6H_2O$, $LiNO_3.3H_2O$, and $Na_2CrO_4.10H_2O$, when used as solvents for the freezing point method, lead to molecular weights for the dissolved substances which are similar to those obtained when water is the solvent, except that when the substance added has an ion in common with the molten hydrated salt, its ionization is prevented either wholly or in part. And when the ions of the dissolved substance are different from those of the solvent, its ionization is apparently unaffected, the molecular weights calculated, not differing materially from those observed in water solutions. In this investigation three other molten hydrated salts, $Ca(NO_3)_2.4H_2O$, $Zn(NO_3).3H_2O$, and $Mn(NO_3)_2.3H_2O$, have been studied as solvents.

The apparatus employed was the one already described by Morgan and Benson, except that a Beckmann thermometer, reading to 0°.01, and set by aid of a normal thermometer, reading to 0°.02, was used throughout. The depressions recorded are each the average of three determinations, agreeing among themselves to 0°.02. Just as with the other salts the separation of the solid phase was induced by infection with a crystal of the pure solvent; and the overcooling was kept below 1° to avoid the necessity of correcting for the fraction of solvent separating as a solid phase.

Determination of the Constants.

For $Ca(NO_3)_2.4H_2O$ the latent heat of fusion is 33.49 gram-calories per gram, according to Pickering[2], so that the freezing point constant can be calculated directly from the relation $K = \frac{0.02T^2}{w}$, where T is the absolute freezing point of the pure solvent, w its latent heat of fusion for 1 g. at that temperature, and K the depression of the freezing point in degrees, caused by the presence of 1 mol. of dissolved substance in 100 g. of the solvent. Since the freezing point of molten $Ca(NO_3)_2.4H_2O$, as determined by us, is 42°.31, we have

[1] This Journal, 29, 1168-75, 1907.

[2] See Landolt-Börnstein-Meyerhoffer. Tabellen. Third ed., p. 470.

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$$K = \frac{0.02\ (273 + 42.31)^2}{33.49} = 59°.41.$$

For neither $Zn(NO_3)_2.3H_2O$, nor $Mn(NO_3)_2.3H_2O$ could the latent heat of fusion be found in the literature, hence it was necessary to determine the values of K by direct observation of the freezing point depressions. For this purpose ammonium nitrate was used as the solute, for it dissolved readily in both solvents, and the work of Morgan and Benson, with molten $LiNO_3.3H_2O$ as solvent, showed it to possess a normal molecular weight when the solvent contained NO_3 ion, *i. e.*, showed that under these circumstances it dissolved in practically the un-ionized state. The freezing point depressions observed for solution of ammonium nitrate, of known strength, in these two solvents are given in Tables I and II, below, the value of K in each case being the depression which would be caused by the presence of 1 mol. (80 g) of ammonium nitrate in 100 g. of the solvent, as calculated by the proportion 80:K::g. per 100:Δ.

IN $Zn(NO_3)_2.3H_2O$ AS SOLVENT. F. P. = 44°.07.

I. Ammonium Nitrate ($M = 80$).

g. NH_4NO_3 per 100	Δ°	K°
1.470	1.071	58.3
2.528	1.830	57.9
3.794	2.773	58.5
5.249	3.910	59.6
	Average	58°.6

Using this average value of K, 58°.6, in the relation $K = \frac{0.02T^2}{w}$, and solving for w, we find the latent heat of fusion of $Zn(NO_3)_2.3H_2O$ to be 34.3 gram-calories per gram at its freezing point 44°.07.

IN $Mn(NO_3)_2.3H_2O$ AS SOLVENT. F. P. = 34°.81.

I. Ammonium Nitrate ($M = 80$).

g. NH_4NO_3 per 100	Δ°	K°
1.063	0.882	66.4
1.492	1.273	68.3
3.052	2.573	67.4
	Average	67°.4

Using this average value of K, 67°.4, in $K = \frac{0.02T^2}{w}$, and solving for w, we find the latent heat of fusion of 1 g. of $Mn(NO_3)_2.3H_2O$ to be 28.09 gram-calories, at its freezing point, 34.81.

Molecular Weights in Solution.

IN $Ca(NO_3)_2.4H_2O$ AS SOLVENT. K = 59°.4. F. P. = 42°.31.

III. Urea ($M = 60$).

g. per 100	Δ°	M
0.9868	1.038	56.5
1.9030	1.920	58.9
2.9900	3.071	57.9

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IV. Ammonium Nitrate ($M = 80$).

g. per 100	Δ°	M
2.280	1.702	79.6
4.789	3.577	79.5
5.644	4.311	77.8

V. Glycol ($M = 62$).

0.9249	0.884	62.2
1.8660	1.779	62.3
2.8080	2.730	61.1
3.6640	3.588	60.7

VI. Acetic Acid ($M = 60$).

1.092	1.078	60.2
2.138	1.995	63.7
3.497	3.006	69.1

IN $Zn(NO_3).3H_2O$ AS SOLVENT. $K = 58°.6$. F. P. $= 44°.07$.

VII. Ethyl Alcohol ($M = 46$).

0.8397	1.083	45.5
1.3500	1.728	45.8

VIII. Methyl Alcohol ($M = 32$).

0.4776	0.843	33.2
0.8198	1.375	34.9
1.141	1.906	35.1
1.461	2.440	35.1
1.814	3.030	35.1
2.448	4.103	35.0

IX. Acetic Acid ($M = 60$).

0.5663	0.550	60.3
1.273	1.188	62.8
2.475	2.236	64.9
3.681	3.197	67.5

X. Acetone ($M = 58$).

0.8435	0.828	59.7
1.7344	1.578	64.4
2.626	2.358	65.3
3.536	3.119	66.4

XI. Formamide ($M = 45$).

1.357	1.442	55.1
2.514	3.195	46.1
3.026	4.180	42.4

XII. Iso-butyl Alcohol ($M = 74$).

1.007	0.757	77.9
2.131	1.611	77.5

IN $Mn(NO_3)_2.3H_2O$ AS SOLVENT. $K = 67°4$. F. P. $= 34°.81$.

XIII. Glycol ($M = 62$).

0.8350	0.938	60.0
1.641	1.858	59.5
2.516	2.893	57.3
3.395	3.929	58.2

XIV. Ethyl Alcohol ($M = 46$).

0.6322	0.732	58.2
1.149	1.448	53.5
2.179	2.793	52.6
3.200	4.240	50.9

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XV. Methyl Alcohol ($M = 32$).

g. per 100	Δ°	M
0.5657	1.149	33.2
1.134	2.225	34.4
1.857	3.575	35.0
2.304	4.320	35.9

XVI. Glycerol ($M = 92$).

0.7927	0.607	88.0
2.062	1.702	81.7
3.394	3.288	69.6

XVII. Acetic Acid ($M = 60$).

0.5902	0.640	62.2
1.247	1.343	62.6
2.593	2.641	66.0

XVIII. Urea ($M = 60$).

1.672	1.676	67.2
2.332	2.356	66.7
3.692	3.574	69.6

It will be observed that the general trend of the molecular weights determined here is similar to that of those determined in $CaCl_2.6H_2O$, $LiNO_3.3H_2O$, and $Na_2CrO_4.10H_2O$, except that in the cases of ethyl alcohol and glycerol in $Mn(NO_3)_2.3H_2O$ (Tables *XIV* and *XVI*), and formamide in $Zn(NO_3)_2.3H_2O$ (Table *XI*) the molecular weights show a decided decrease with increased concentration. As soon as sufficient data of this sort are at hand, a quantitative study of the thermal relations of these solutions will be made, in order, if possible, to test the effect of the heat of dilution upon the molecular weight, as calculated by the freezing point law, the possible effect of which has already been sketched by Morgan and Benson[1].

Summary.

The results of this work may be summarized as follows:

1. The freezing point constants of molten $Ca(NO_3)_2.4H_2O$, $Zn(NO_3)_2.3H_2O$, and $Mn(NO_3)_2.3H_2O$ are respectively: 59°.4(F. P. =42°.31); 58°.6(F. P. = 44°.07), and 67°.4(F. P. = 34°.81).

2. The heats of fusion for 1 g. each of $Zn(NO_3)_2.3H_2O$ and $Mn(NO_3)_2.3H_2O$, as calculated from the experimentally determined values of K, and the relation $w = \frac{0.02T^2}{K}$, are respectively 34.3 gram-calories at freezing point, 44°.07, and 28.09 gram-calories at the freezing point, 34.°81.

LABORATORY OF PHYSICAL CHEMISTRY,
August, 1907.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 143].

PLATINUM RESISTANCE FURNACE FOR MELTING POINTS AND COMBUSTIONS.

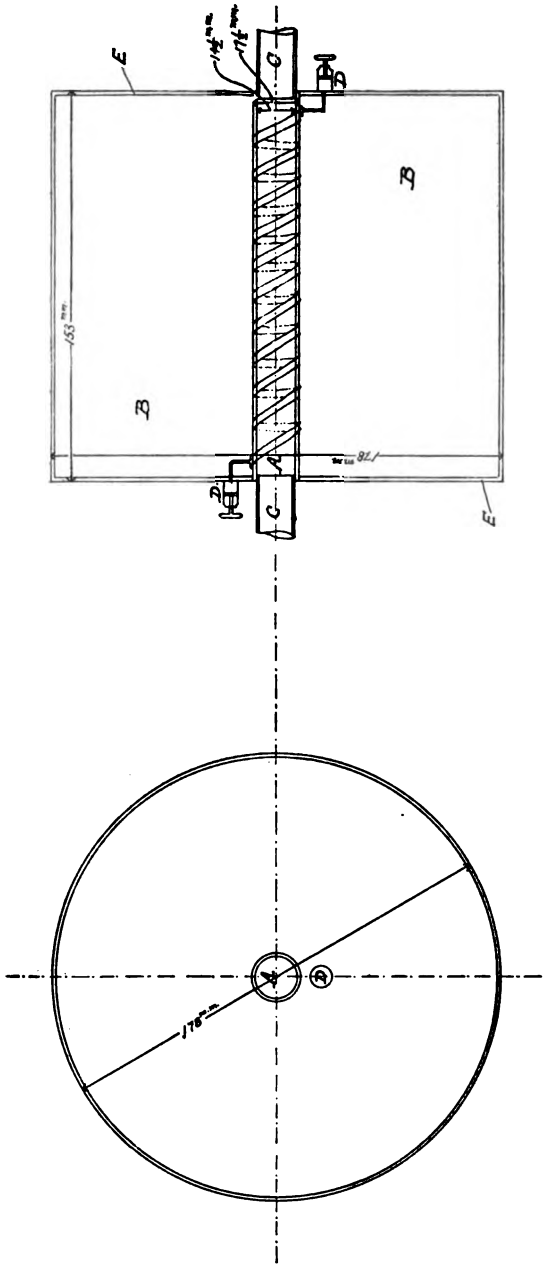
By SAMUEL A. TUCKER.

Received June 28, 1907.

The small furnace here described was the outcome of some work in

[1] Loc cit.

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connection with the combustion of carbides in chlorine, and was found very useful for combustions requiring high temperatures. It subsequently

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proved applicable to melting point determinations up to 1200°, such as those of copper mattes, etc.

The furnace consists of a quartz tube A, wound with platinum tape. The figure gives the side and end elevations. With the dimensions as shown, the tape was 51 cm. long, 6 mm. wide, and 0.06 mm. thick. The ends of the tape were welded to short pieces of No. 12 S. W. G. platinum wire to serve as leads, and the tape was held in position by asbestos cord binding.

The containing walls E, are of sheet asbestos, which is easily made to the shape shown, two disks for the ends being cemented to the cylinder. All the joints were cemented with "asbestos cement", which holds the pieces very firmly and takes but a few minutes to set.

The wires leading in were connected to suitable binding posts D, and the open space B, between the quartz tube and containing walls was filled with infusorial earth. At the temperatures possible with this furnace, infusorial earth makes the best heat insulating material, and its use makes it possible to construct a relatively large furnace of light weight.

The construction would have been better if a longer quartz tube had been used, but at the time that it was made this was impossible to procure, and it necessitated joining in Jena glass tubes C, for use in combustion work. The glass tubes were easily joined to the quartz by the same cement.

For use in melting point determinations the glass tubes are removed, the furnace being set up on one end and a plug of asbestos placed in the tube making a seat for a small graphite crucible which rests on the middle portion of the tube.

The material is then placed in the crucible together with the junction of a thermo-couple, and the material melted by raising the current gradually.

The following gives the energy required for higher temperatures for melting point determinations:

Minutes	Amperes	Volts	Temperature
4	30	14	1280°
6	25	11.8	1310
7	"	"	1320
12	"	"	1190
15	"	11	1170
23	"	"	1170
45	"	"	1180

For combustions, a temperature of 800° is obtained with 18 amperes, the drop across the furnace being 9 volts.

Higher temperature for melting point determinations are obtained with 25 amperes at 11 volts, which gives a temperature of 1180° and with 30 amperes at 14 volts a temperature of 1300° may be reached.

ELECTROCHEMICAL LABORATORY, COLUMBIA UNIVERSITY,
May 29, 1907.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY].

NEW RESULTS IN ELECTRO-ANALYSIS.[1]

BY THOMAS P. MCCUTCHEON, JR.

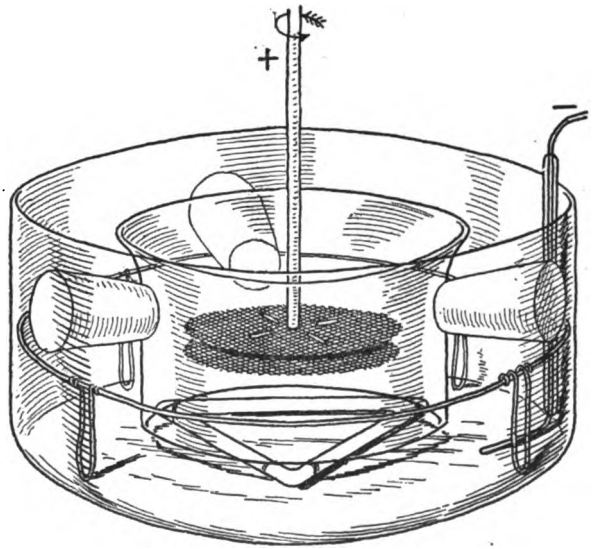
Received August 15, 1907.

Previous workers in electro-chemical analysis have directed their efforts almost entirely to the determination and separation of metals. A year ago, J. H. Hildebrand[2], working in this Laboratory, showed that such anions as Br, I, PO_4, $Fe(CN)_6$, CNS could be determined in the electrolytic way. He employed the mercury cathode and an attackable silver anode in a cell especially devised for the purpose. Sodium and potassium can be determined simultaneously, so that a complete analysis of such salts as sodium chloride and potassium ferrocyanide can now be made with ease and accuracy.

The purpose of the first part of this investigation was to extend this work to the estimation of other anions and to learn whether other metals than silver could be advantageously used as anodes. In the second part of the work, the same form of cell was used in the separation of certain metals.

Apparatus.

The decomposition cell, devised by Hildebrand, consisted of a crystallizing dish, the bottom of which was covered with a layer of mercury. In-



side of this was placed a beaker of smaller diameter, without a bottom and supported so that its lower edge extended just below the surface of the mercury. The inner cup was held in position by means of three

[1] From author's thesis for Ph. D. degree, 1907.

[2] This Journal, 29, 4, 447.

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corks placed radially. The mercury was connected with the cathode by means of a stout platinum wire enclosed in a glass tube.

The inner compartment contained the solution to be analyzed. Water was placed in the outer compartment, to which a few drops of sodium chloride solution were added to increase the conductivity and a nickel wire to aid in the decomposition of the amalgam.

The anode consisted of two disks of platinum gauze, placed one above the other and supported by a platinum rod. It was plated with silver by making it the cathode in a bath of silver potassium cyanide. It was then washed, dried and weighed. It was rotated 250-300 times per minute by means of a small motor. The anode was lowered into the inner compartment until the upper gauze was covered by the solution.

The procedure for the analysis of such a salt as sodium chloride was as follows: the salt was placed in the inner compartment and diluted to about 50 cc. and the anode placed in position, while in the outer compartment, as stated above, pure water was placed and a little sodium chloride solution so that the current would be conducted more rapidly at first. On electrolyzing the sodium chloride in the inner compartment, the sodium passed into the mercury and formed an amalgam. In a short time this amalgam found its way into the outer compartment, where it was decomposed with formation of sodium hydroxide. At the conclusion of the experiment the sodium hydroxide was estimated by titration with standard acid, using methyl orange as indicator. The chlorine appeared as silver chloride at the anode and was perfectly adherent. As nothing remained in the inner compartment but pure water, the needle of the ammeter gradually fell almost to zero. This indicated the end of the experiment and the anode was removed, dried and weighed. The increase in weight represented the chlorine in the sodium chloride.

Experimental Part.

On experimenting with other anions than those mentioned above, it appeared that the silver anode was unsatisfactory. In some cases, as with borate and sulphide, the silver salt formed was not perfectly adherent; silver fluoride, on the other hand, was somewhat soluble in water. The following experiments were instituted, with these facts in mind, in the hope that other anodes than silver might prove helpful.

Lead Anode.

The platinum gauzes were plated with lead in a bath of lead sulphocyanide dissolved in potassium hydroxide. In the experiments to be described 4-5 volts were used. This ordinarily gave a current of about 0.5 ampere, falling to 0.02-0.01 ampere when the salt was completely removed from the inner compartment. The anode was rotated 250 times per minute.

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Potassium Cyanide.—White lead cyanide formed readily, but did not adhere to the anode.

Borax.—Amperes 0.7-0.03. The lead borate was non-adherent.

Potassium Fluoride.—Amperes 0 7-0.01. After many trials it was again found impossible to obtain a satisfactory deposit. A considerable amount of lead peroxide formed on the anode.

Sodium Sulphate.—Some lead sulphate formed on the anode, but the formation of lead peroxide prevented the estimation of SO_4. By titrating the caustic soda formed in the outer compartment, it was possible to determine the sodium in the salt with fair results.

	Grams	Amperes	Volts	Time, min.
Sodium sulphate present	0.0852		..	..
" "	0.0276	0.1-0.01	5	30
" found	0.0274		..	..
	0.0274		..	..
	0.0276		..	..

Sodium Sulphide.—The lead anode became black as soon as placed in the solution of sodium sulphide. However, as the electrolysis proceeded, pieces of the lead sulphide became detached, making an exact estimation of the sulphur impossible. A curious phenomenon was noticed during this experiment. The solution of sodium sulphide used was quite colorless. In a few minutes the solution in the inner compartment took on a very pronounced yellow color. The same color was noticed when cadmium and bismuth anodes were used with soluble sulphides. The cause of this color will shortly receive further investigation.

Cadmium Anode.

The anode was plated in a bath of potassium cadmium cyanide.

Sodium Sulphide.—The formation of yellow cadmium sulphide became apparent before the current was passed. The solution in the inner compartment became yellow, but after a few minutes became colorless again. The deposit of cadmium sulphide on the anode was adherent, if carefully handled. It was dried in an oven at 115° and weighed. A low voltage should be used and care be taken not to rotate the anode too rapidly; otherwise small pieces of cadmium sulphide may become detached.

	Grams	Volts	Amperes	Time, min.
Sodium sulphide present	0.0429	..		..
" "	0.0252	3.5	0.1-0.03	15
" found	0.0252	..		..
	0.0256	..		..
	0.0251	..		..

Sodium Chromate.—The cadmium chromate was gelatinous and non-adherent.

Sodium Arsenate.—White cadmium arsenate formed abundantly, but did not adhere to the anode.

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Bismuth Anode.

The anode was plated from a solution of bismuth nitrate containing sulphuric acid.

Sodium Chromate.—The color of the liquid in the inner compartment altered from yellow to green and finally a green gelatinous precipitate separated, probably chromium hydroxide. No bismuth chromate formed on the anode.

Sodium Sulphide.—The liquid in the inner compartment again became yellow. When a high pressure was used (14 volts) black bismuth sulphide separated from the liquid. Little bismuth sulphide formed on the anode.

Sodium Arsenate.—No bismuth arsenate appeared, indicating that the bismuth was not attacked by the arsenate anion. The liquid in the inner compartment became acid to litmus, probably due to the formation of arsenic acid.

Sodium Iodide.—The solution in the inner compartment assumed a deep orange color at first. On continuing the electrolysis the color became much paler. The bismuth anode did not change in appearance.

Zinc Anode.

The anode was plated from a solution of sodium zincate.

Sodium Phosphate.—White zinc phosphate formed, but did not adhere.

Sodium Tungstate.—When the anode was rotated slowly, the surface of the mercury in the inner compartment took on a blue iridescent tarnish. No hydrogen was evolved in the outer compartment and the current did not fall. Rapid rotation of the anode caused a slight evolution of hydrogen in the outer compartment and a non-adherent, white, flocculent precipitate, probably zinc tungstate, formed in the inner compartment. In the latter case the current fell from 0.1-0.01 ampere. Five volts were used in each case.

Potassium Cyanate.—A white, non-adherent precipitate formed.

Further a copper anode was used with a solution of sodium arsenite. The green arsenite of copper was formed readily, but little of it adhered to the anode. When an iron anode was used with potassium ferrocyanide, the anode was not attacked and hydroferrocyanic acid seemed to form in the inner compartment.

It is clear, then, that the anodes, described above, behave in several ways toward the different anions. In some cases an insoluble precipitate is formed which may or may not adhere to the anode. In other cases, for example, the iron anode with a soluble ferrocyanide, the anode is not attacked, but the free acid is generated.

These experiments, while not at all exhaustive, seem to indicate that silver is the most suitable anode for receiving most anions. It is entirely

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probable that further study will reveal conditions under which the other anodes will give good results.

Electrolysis of Solutions of Metallic Chlorides with a Silver Anode. Up to this time only salts of sodium and potassium had been electrolyzed in this apparatus. Attention was next turned to other metals, using their chlorides with a silver anode, to learn whether they formed amalgams and whether the amalgams, if formed, decomposed in the outer compartment with formation of hydroxides. A solution of calcium chloride was placed in the inner compartment and electrolyzed in the usual manner. From the appearance of the surface of the mercury it was evident that an amalgam was formed at first, but in a short time it decomposed in the inner compartment, giving rise to a large quantity of calcium hydroxide. H. S. Lukens, working in this laboratory at the same time, found that the amalgams of barium and strontium deported themselves like those of sodium and potassium and decomposed in the outer compartment with formation of hydroxide. He succeeded in making a complete analysis of barium chloride, weighing the chlorine collected at the anode and titrating the barium hydroxide formed in the outer compartment in the manner to be described later. These facts seemed so suggestive that solutions of a number of the metallic chlorides were made up and electrolyzed with the following results:

Amalgams of lithium, sodium, potassium, calcium (see below), strontium and barium decompose in the outer compartment with formation of the corresponding hydroxides.

Amalgams of cadmium, tin, antimony, iron, aluminium, chromium, manganese, zinc, nickel, cobalt, titanium, vanadium, zirconium, thorium, lanthanum, cerium, neodymium, praseodymium, magnesium and uranium decompose in the inner compartment with formation of hydroxides.

Electrolysis of Cerium Chloride. A peculiar result was observed on electrolyzing a solution of cerous chloride. At the beginning the appearance of the surface of the mercury indicated the formation of an amalgam. A subsequent examination proved conclusively that considerable cerium had passed into the mercury. Later the solution in the inner compartment took on a pink color, which finally resembled a somewhat dilute solution of potassium permanganate. This color was observed by transmitted light. It had a greenish, fluorescent appearance by reflected light. The solution was filtered without losing any of its properties. Addition of common salt produced a brownish red precipitate, which differed in appearance both from the hydrated dioxide of cerium, produced by conducting chlorine into an alkaline cerous salt and from the hydrated trioxide, produced by the action of ammonia and hydrogen peroxide on a cerous salt. The precipitate did not dissolve readily in hydrochloric acid, but dissolved in concentrated sulphuric acid with a yellow color.

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In this latter respect it resembled the dioxide. The same precipitate formed on allowing the purple solution to stand several days or on continuing the electrolysis for about an hour. A pressure of 8 volts seemed to be most favorable for the formation of this compound. It appeared to be a derivative of cerium in a colloidal condition. A further study of this compound will be made immediately.

Electrolysis of Calcium Chloride. A more careful study was next made of the behavior of calcium chloride in the cell. Lukens found that the salt with which we had been working was contaminated with considerable amounts of magnesium. The calcium was purified by a number of precipitations as oxalate. On electrolyzing the pure chloride, he found that a part of the calcium appeared in the outer compartment like strontium and barium. He was never able to obtain all of it. On mixing magnesium chloride with it again, none of the calcium appeared outside. With these facts in mind, Lukens made a mixture of barium, calcium and magnesium chlorides and was able to completely separate the barium from the calcium and magnesium. A determination by the writer gave the following result:

	Grams.	Volts	Amperes	Time, hours
Barium chloride	0.1049	...		..
" present	0.0691	3.5	0.5–0.02	2
" found	0.0692	(in presence of calcium and magnesium chlorides.)		

All the previous work had been done with a pressure of 5 volts or under. It seemed probable to the writer that by using a higher voltage, all the calcium could be removed to the outer compartment. The following examples show that such is the case:

	Grams.	Volts	Amperes	Time, hours
Calcium chloride	0.0771	..		..
" present	0.0278	8	0.1–0.02	2
" found	0.0272	..		..
	0.0280	...		..
	0.0278	..		..
	0.0276	..		..
	0.0280	..		..

The estimation of the calcium was troublesome at first, as the calcium hydroxide which separated in the outer compartment was not readily soluble in standard acid of convenient strength. The difficulty was removed by adding to the solution in the outer part of the cell a slight excess of standard hydrochloric acid at the beginning of the experiment. At the conclusion the excess of acid was estimated with standard sodium carbonate solution, using methyl orange as indicator.

Separation of Calcium from Magnesium. By using a still higher pressure it was found possible to separate calcium from magnesium, although considerable time was necessary. To remove the last traces of calcium

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it was found advantageous to add a drop of hydrochloric acid to the solution in the inner compartment from time to time.

	Grams.	Volt	Amperes	Time, hours
Magnesium chloride	0.1000	..		..
Calcium chloride	0.0771	9	0.3–0.02	3
" present	0.0278	..		..
" found	0.0282	..		..
	0.0276	..		..
	0.0281	..		..

The calcium hydroxide could be titrated directly in the outer compartment as described above, but to obtain accurate results it was necessary to stir the mercury a long time with a glass rod tipped with a piece of rubber to completely decompose the amalgam. It was found more convenient to remove the anode, siphon out the liquid in the inner compartment with the magnesium hydroxide formed there, and wash the inner compartment thoroughly with pure water. The remaining contents of the cell were then poured into a large beaker. After stirring the mercury well, the titration could be made without difficulty. This procedure was followed in all subsequent analyses where an insoluble hydroxide was formed in the inner compartment.

Separation of Barium and Calcium from Magnesium. The thought occurred that by mixing barium, calcium and magnesium chlorides, it would be possible to remove the barium to the outer compartment with a low pressure, estimate it and then remove the calcium by increasing the pressure. Time did not permit of the completion of this work, but a single determination will show that the separation may be realized:

	Grams.	Volts
Barium chloride	0.1049	...
Calcium "	0.0771	...
Magnesium "	0.1000	...
Barium present	0.0691	...
" found	0.0691	3.5
Calcium present	0.0278	...
" found	0.0274	9

Separations.

In view of the fact that the amalgams of the metals divide themselves into two classes, some decomposing in the outer and some in the inner compartment, attention was directed to separations. Obviously there is the possibility of separating any metals in the first class from any metal in the second class and in most of the cases tried the separation proved a success. The only aim in this investigation was to discover whether the separations could be made. No effort was made to reduce the time factor. The experiment was usually begun at two o'clock and stopped between five and six. Nor was an effort made to use larger quantities of the metals. This would materially decrease the percentage

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error. In order to work with larger quantities it may be found advantageous to use anodes with a larger surface. These points will be worked out in detail and the most favorable conditions found for each separation.

Separation of the Alkalies and Alkaline Earths from Uranium.

These separations are usually troublesome, and it was thought that an electrolytic separation might be useful.

Sodium from Uranium. No difficulty was experienced in this or the following separation, although the uranium exercised a retarding influence on the sodium. Silver chloride formed on the anode as usual and the inner compartment became full of yellow uranium hydroxide, which later became black. The sodium hydroxide in the outer compartment was titrated with standard hydrochloric or sulphuric acid.

	Grams.	Volts	Amperes	Time, hours
Uranium chloride	0.1000	...		..
Sodium chloride	0.1172	..		..
" present	0.0461	3–5	0.3–0.02	3
" found	0.0463	...		..
	0.0459	...		..
	0.0457	...		..

POTASSIUM FROM URANIUM.

	Grams.	Volts	Amperes	Time, hours.
Uranium chloride	0.1000	...		..
Potassium "	0.1467	3–5	0.5–0.01	2
" present	0.0768	...		..
" found	0.0771	...		..
	0.0771	...		..
	0.0766	...		..

Lithium from Uranium. As lithium chloride had not been previously analyzed in this cell, a solution was made up and electrolyzed with the following results:

	Grams.	Volts	Amperes	Time, hours
Lithium chloride	0.0846	..		..
" present	0.0140	5	0.03–0.02	2
" found	0.0143	..		..
	0.0143	..		..
	0.0144	..		..

The separation was made as for sodium and potassium from uranium.

	Grams.	Volts	Amperes	Time, hours
Uranium chloride	0.1000	5	0.03–0.02	2
Lithium chloride	0.0846	..		..
" present	0.0140	..		..
" found	0.0143	..		..
	0.0142	..		..
	0.0141	..		..
	0.0141	..		..
	0.0142	..		..
	0.0143	..		..

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Barium from Uranium. In this separation the addition of a few drops of hydrochloric acid during the electrolysis was necessary to separate the last traces of barium from the uranium. As under calcium, a slight excess of standard acid was added to the solution in the outer compartment at the beginning of the experiment to prevent the formation of insoluble barium hydroxide. The excess of acid was estimated with standard alkali.

	Grams.	Volts	Amperes	Time, hours
Uranium chloride	0.1000	..		..
Barium chloride	0.1040	5	0.15–0.01	1
" present	0.0685	..		..
" found	0.0685	..		..
	0.0688	..		..
	0.0682	..		..
	0.0682	..		..

Strontium from Uranium. In this separation strontium bromide was used.

	Grams.	Volts	Amperes	Time, hours
Uranium chloride	0.1000	..		..
Strontium bromide	0.1456	5	0.4–0.02	2
" present	0.0513	..		..
" found	0.0513	..		..
	0.0513	..		..
	0.0516	..		..
	0.0510	...		..

Separation of Barium from Thorium, Cerium, Lanthanum and Neodymium.

The following separations were made to further test the applicability of the method. As before, traces of barium were apt to remain with the hydroxide in the inner compartment unless a few drops of hydrochloric acid were added during the electrolysis.

BARIUM FROM THORIUM.

	Grams.	Volts	Amperes	Time, hours
Thorium chloride	0.1300	..		..
Barium chloride	0.1049	5	0.4–0.02	2
" present	0.0691	..		..
" found	0.0689	..		..
	0.0691	..		..
	0.0689	..		..

BARIUM FROM CERIUM.

	Grams.	Volts	Amperes	Time, hours
Cerium chloride	0.1000	..		..
Barium chloride	0.1040	5	0.4–0.02	2
" present	0.0685	..		..
" found	0.0685	..		..
	0.0684	..		..
	0.0686	..		...

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BARIUM FROM LANTHANUM.

	Grams.	Volts	Ampere	Time, hours
Lanthanum chloride	0.0500	..		..
Barium chloride	0.1049	5	0.3–0.01	
" present	0.0691	..		..
" found	0.0693	..		..
	0.0689	..		..

BARIUM FROM NEODYMIUM.

	Grams.	Volts	Amperes	Time, hours
Neodymium chloride	0.1500	...		..
Barium chloride	0.1049	5	0.5–0.01	2
" present	0.0691	...		..
" found	0.0693	..		..
	0.0690	..		..
	0.0693	..		..

Thallium.

The similarity of thallium to the alkalies in many of its behaviors raised the hope that its amalgam would decompose in the outer compartment of the cell. Owing to the insolubility of thallous chloride, the sulphate was used in connection with a lead anode. The platinum gauze was plated with lead in a very satisfactory manner by making it the cathode in a bath of hydrofluosilicic acid. The anode was a strip of pure lead.

When thallous sulphate was electrolyzed in the cell, the solution in the outer compartment soon gave a very distinct test for thallium with potassium iodide. While no quantitative results can be given as yet, it is hoped that thallium can be estimated in this way and its separation from other metals accomplished.

Ammonium Chloride.

A solution of ammonium chloride was electrolyzed with a silver anode. An amalgam was formed in the inner compartment, which swelled up enormously. It was interesting to note that the surface of the mercury in the outer compartment became covered with bubbles and the solution showed a strong alkaline reaction, indicating that the ammonium amalgam had passed to the outer compartment like the amalgams of sodium and potassium.

Electrolysis of a Mixture of Sodium and Potassium Chlorides.

The following experiments were made to ascertain whether larger amounts of chlorine than formerly used could be estimated with the present form of anode. Hildebrand used a solution of sodium chloride containing 0.0708 grams of chlorine. In these determinations double the amount was estimated with an error of less than 0.0005 gram.

The method might be used in the estimation of a mixture of sodium and potassium as chlorides. The mixed chlorides could be weighed, dissolved in water and electrolyzed. The chlorine could be weighed and

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the combined sodium and potassium titrated in the outer compartment. The sodium and potassium could be readily calculated from these data.

	Grams.	Volts	Amperes	Time, min.
Sodium chloride	0.1166			..
Potassium chloride	0.1478	3.5–5	0.5–0.02	45
Chlorine present	0.1416			..
" found	0.1420			..
	0.1420			..
	0.1418			..
	0.1420			..
	0.1414			..

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY].

THE ELECTROLYSIS OF THE HALIDES OF THE ALKALINE EARTH METALS.

BY HIRAM S. LUKENS AND EDGAR F. SMITH.

Received August 15, 1907.

The studies made by Hildebrand and more recently by McCutcheon with the form of cell pictured and described[1] and in which the rotating silver anode and mercury cathode are employed, led us to try out certain lines of thought in the same way. For example, it seemed worth the while to learn just what quantities of barium chloride, let us say, could be electrolyzed in the Hildebrand cell and the analyst be sure of the accuracy of the results both with respect to the barium and the associated halogen. It was very soon found that quantities of barium chloride exceeding 0.2 gram could be electrolyzed with satisfaction in the course of from forty to sixty minutes with a current of 0.3 ampere and from 3.5 to 4 volts. The anode made 300 revolutions per minute.

The appended results appear in the order in which they were obtained.

Barium present in gram.	Barium found in gram.	Chlorine present in gram.	Chlorine found in gram
0.2277	0.2276	0.1180	0.1177
0.2277	0.2274	0.1180	0.1178
0.2277	0.2277	0.1180	0.1181
0.2277	0.2278	0.1180	0.1180
0.2277	0.2277	0.1180	0.1180
0.2277	0.2277	0.1180	0.1181

In the electrolysis of strontium bromide, the determination of the bromine was omitted. This halogen adhered firmly to the rotating silver anode to which it attached itself. It was, however, not weighed. The determination of metal alone was made.

Strontium present in gram.	Strontium found in gram.
0.0727	0.0725
0.0727	0.0727
0.0727	0.0727
0.0727	0.0726
0.0727	0.0726

[1] This Journal, **29**, 447.

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The current was of the same strength as given under barium chloride. The time required was also practically the same.

It was perfectly natural to wish to learn how calcium chloride would conduct itself, although it seemed that it could not fail to behave like its analogues. To our great surprise the amalgam formed in the inner compartment did not diffuse into the outer, larger dish, and there decompose, but contrariwise, it decomposed in the inner vessel forming there a mass of hydroxide. Calcium could not be detected in the outer vessel where the alkalies and barium and strontium appeared as amalgams. decomposed and were determined. Instead of seeking to solve the mystery of this behavior of the calcium amalgam, at that moment, we decided to study the electrolysis of pure magnesium chloride. Upon doing this, large quantities of magnesium hydroxide formed in the inner compartment, while not a trace of magnesium could be detected in the outer vessel. Perhaps then the presence of magnesium chloride in the calcium chloride, which had been electrolyzed with the unexpected result of formation of calcium hydroxide in the inner chamber, was in a measure responsible for this undesired behavior? Accordingly the calcium chloride, employed in the electrolysis, was examined for magnesium. It showed it in abundance. When calcium chloride, free from every trace of magnesium, was subjected to electrolysis, it behaved like the halides of the alkali metals, and like those of barium and strontium, *i. e.*, its amalgam passed into the outer compartment of the cell and was there decomposed and the calcium hydroxide determined.

The next step consisted in bringing together known amounts of pure calcium chloride and pure magnesium chloride, and subjecting the mixtures to electrolysis. The proportions of magnesium varied in amount from one-half to equal that of the calcium. The dilution of the solutions was the same as in all previous experiments. It never exceeded 30 cc. The pressure varied from 3.5 to 4 volts, while the time period did not extend beyond an hour.

In all such trials the results were identical. The inner cup was filled with insoluble hydroxide and in the outer compartment not a trace of calcium or magnesium was detectible. It seemed possible then, to restrain the calcium by merely adding magnesium chloride to its salt solution undergoing electrolysis. Could not calcium be separated in this electrolytic way from magnesium? Evidently not, under the conditions previously outlined. It remained, however, for McCutcheon to show how that separation could be successfully performed. That, however, came later.

At this period of our experimentation the retention of the calcium by the magnesium suggested very promptly the separation of certain other metals from calcium and magnesium. The subjoined records disclose our line of thought.

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Separation of Sodium and Potassium from Calcium and Magnesium.— A solution containing as chlorides :

0.0222 gram of calcium,
0.0210 " " magnesium, and
0.0474 " " sodium,

was electrolyzed for a period of fifty minutes with a current of 0.25 ampere and 3.5 volts. The calcium and magnesium amalgams decomposed in the inner cup with the formation of their hydroxides, while the sodium amalgam sustained a like decomposition in the outer compartment, where the sodium hydroxide formed was determined by titration with N/10 hydrochloric acid :

Sodium found in grams.
0.0471
0.0474
0.0472
0.0474
0.0476
0.0474

On substituting potassium chloride for sodium chloride in the mixture with calcium and magnesium chlorides, and exposing the same to electrolysis under conditions similar to those just given, the amount of potassium separated and determined was :

Potassium found in gram.	Potassium present in gram
0.0582	0.0580
0.0583	0.0580
0.0580	0.0580
0.0579	0.0580
0.0580	0.0580
0.0580	0.0580

The alkali metals may, therefore, be readily and accurately separated from calcium and magnesium in the electrolytic way.

Separation of Barium and Strontium from Calcium and Magnesium.— In attempting the separation of barium from calcium and magnesium the solution contained the following quantities of the three metals as chlorides :

0.0222 gram of calcium
0.0210 " " magnesium
0.0455 " " barium.

A drop of dilute hydrochloric acid was added to the solution in the inner compartment, and the mixture was then electrolyzed with a current of 0.3 ampere and 3.5 to 4 volts. The halogen attached itself firmly to the rotating silver-plated anode, calcium and magnesium amalgams were formed but speedily decomposed in the inner compartment, while the barium amalgam passed to the outer vessel, where it decomposed to hydroxide, which upon titration showed the presence of

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1	0.0456	gram	of	barium
2	0.0455	"	"	"
2	0.0454	"	"	"
4	0.0454	"	"	"
5	0.0455	"	"	"
6	0.0454	"	"	"
7	0.0454	"	"	"

When the quantity of barium was doubled (0.910 gram), the quantities obtained were:

1	0.0911	gram
2	0.0910	"
3	0.0912	"
4	0.0910	"

Upon substituting strontium bromide for barium chloride in the mixture of chlorides and electrolyzing the solution under the same conditions as previously the results were:

Strontium present in grams.	Strontium found in grams.
0.0565	0.0563
0.0565	0.0565
0.0565	0.0564
0.0565	0.0565
0.0565	0.0566
0.0565	0.0565

Separation of Barium and Strontium from Magnesium alone.—These separations were conducted with conditions like those given under the mixtures in which calcium was also present.

Barium present in grams.	Magnesium present in grams.	Barium found in grams.
0.0455	0.0358	0.0455
0.0455	0.0358	0.0456
0.0455	0.0358	0.0455
0.0455	0.0358	0.0455
0.0455	0.0358	0.0456
0.2277	0.0358	0.2277
0.2277	0.0358	0.2275
0.2277	0.0358	0.2277

Strontium present in grams	Magnesium present in grams	Strontium found in grams
0.0221	0.0358	0.0220
0.0221	0.0358	0.0222
0.0221	0.0358	0.0221
0.0221	0.0358	0.0221
0.0221	0.0358	0.0220

Separation of the Alkali and Alkaline Earth Metals from Iron and Aluminium.—In the separation of barium from iron the chlorides, as in all other instances, were employed. The conditions prevailing here were identical with those observed in the preceding experiments. The iron amalgam, if produced, decomposed almost immediately with the forma-

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tion of ferric hydroxide in the inner compartment, while the barium passed to the outer chamber and there underwent decomposition. The current equaled 0.3 ampere and 3 to 5 volts. The time period did not exceed fifty minutes.

Barium present	Iron present	Barium found
0.0455	0.0276	0.0452
0.0455	0.0276	0.0454
0.0455	0.0276	0.0455
0.0455	0.8276	0.0456
0.0455	0.0276	0.0455
0.0455	0.0276	0.0455

Strontium present		Strontium found
0.0565	0.0276	0.0564
"	"	0.0565
"	"	0.0562
"	"	0.0565

Potassium present		Potassium found
0.0580	0.0276	0.0579
"	"	0.0581
"	"	0.0580
"	"	0.0581
"	"	0.0582

Sodium present		Sodium found
0.0474	0.0276	0.0471
"	"	0.0475
"	"	0.0474
"	"	0.0473
"	"	0.0474
"	"	0.0474

Barium present	Aluminium present	Barium foun
0.0455	0.0199	0.0454
"	"	0.0453
"	"	0.0455
"	"	0.0455
"	"	0.0453
"	"	0.0455

Strontium present		Strontium found
0.0221	0.0199	0.0220
"	"	0.0220
"	"	0.0221
"	"	0.0220
"	"	0.0221
"	"	0.0221

Potassium present		Potassium found
0.0580	0.0199	0.0582
"	"	0.0581
"	"	0.0580
"	"	0.0579
"	"	0.0580
"	"	0.0580

Sodium present		Sodium found
0.0474	0.0199	0.0474
"	"	0.0474
"	"	0.0475
"	"	0.0474
"	"	0.0474
"	"	0.0473

In none of these separations has there been an effort made to ascertain

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the exact decomposition pressure of any particular chloride. This was not done in the study carried out by Hildebrand (*loc cit.*). This point is receiving attention at present in this laboratory, more especially in the determination and separation of anions by use of a silver or some other suitable anode.

A very interesting feature of the particular studies here described as well as a portion of those communicated by McCutcheon (p. 1449) is that by the current, applied as it has been in this laboratory, many interesting separations are now possible in the groups of the alkali and alkaline earth metals. Even inexperienced persons can carry out such separations. Further, many of these surpass the ordinary gravimetric procedures both in accuracy and in the short time necessary for their execution.

The analyst is not restricted any longer, in the application of the current in analysis, to the determination of such metals as copper, nickel, zinc, lead, etc. The field is now vastly broader. Anions may be most accurately determined and probably be separated in many instances more successfully than in any other way. While not desiring to anticipate another investigation now in progress, it may be mentioned that in plating anodes like those used in the present study and by McCutcheon, and by Hildebrand in their particular researches, with a suitable, adherent coating, such as calcium hydroxide, soluble fluorides may be electrolytically analyzed in the cell used in this laboratory, with the outcome that both the anion, fluorine, and the cation, sodium, can be most accurately determined. What further progress in this field may bring, one can scarcely say, yet in the language of the immortal Faraday we may rest assured " that advancement in it, whether in degree great or small, instead of exhausting the subject of research, will open doors to future and more abundant knowledge, overflowing with beauty and utility to those who will be at the * * * * * pains of undertaking its experimental investigation."

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ELECTROLYSIS OF METALLIC CHLORIDE SOLUTIONS WITH THE USE OF ROTATING SILVER ANODE AND MERCURY CATHODE.

BY THOMAS P. MCCUTCHEON JR. AND EDGAR F. SMITH.

Received August 15, 1907.

In previous communications it has been shown how readily certain bodies, *e. g.*, barium chloride, may be electrolyzed in the cell of Hildebrand.[1] It occurred to us that a study of metallic halides, in general, might reveal something of interest. To this end solutions of chlorides, as neutral as they could be obtained, were made up so that in a dilution of 50 cubic

[1] This Journal, 29, 447.

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centimeters there was present approximately 0.1 gram of metal. The anode made about 200 revolutions per minute. The pressure equaled, unless otherwise stated, 8 volts.

On introducing a solution of cerous chloride into the inner compartment and arranging the cell as usually done it was noticed that at the beginning, on applying a current of 0.8 to 0.02 ampere and from 8 to 10 volts, a cerium amalgam was formed. This was evident from the appearance of the surface of the mercury cathode. After the chlorine had gone to the anode of silver and the current had fallen to about 0.5 ampere, the amalgam began to decompose and the solution in the inner compartment became red in color by transmitted light (like potassium permanganate), while by reflected light a greenish fluorescence, as seen in crude petroleum, was distinctly visible. This solution lost none of its properties on filtering. On the addition of common salt it gave a reddish brown precipitate, indicating that the liquid contained some colloidal cerium compound.

The fact that in the course of the electrolysis the current fell to 0.2-0.01 ampere would indicate that the cerium compound, in the solution, was not ionized. On allowing the electrolysis to continue for some time after the ammeter had fallen to 0.02 ampere, the colloid separated completely in the form of a reddish brown precipitate which floated about in the agitated water.

REACTIONS OF THE COLLOIDAL CERIUM SOLUTION.

Ammonia	brownish red precipitate.
Sodium Chloride	" " "
Potassium Hydroxide	dilute solution was added slowly,—the cerium solution became almost colorless, a slight brownish tint, no precipitate. After adding potassium permanganate and treating with ammonia, a precipitate formed resembling cerous hydroxide.
Potassium Chromate	brownish red precipitate.
Potassium Iodide	" " "
Stannous Chloride	" " "
Hydrogen Peroxide	" " "
" "	and ammonia, yellow precipitate resembling the hydrated dioxide of cerium.

When dilute sulphuric acid and potassium iodide were added to the colloidal solution and the liquid warmed, the brownish red precipitate separated at first, after which iodine was liberated and was collected in carbon bisulphide. This reaction is characteristic of cerium dioxide.

On warming the colloidal solution with dilute sulphuric acid and al-

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cohol, the odor of aldehyde was evident. These two reactions reduce cerium dioxide to the sesquioxide.

In concentrated sulphuric acid the colloidal solution became yellow in color. Upon adding ferrous sulphate and then ammonium hydroxide, a precipitate of ferric hydroxide separated, showing that the colloidal solution possessed oxidizing action.

The reddish brown precipitate a mixture of oxides.—While cerous hydroxide is not readily or completely soluble in hydrochloric acid, and yellow hydrated dioxide of cerium, (made by passing chlorine into cerous hydroxide, suspended in caustic soda), dissolves easily in hydrochloric acid, the red hydrated trioxide of cerium (made by the action of ammonia and hydrogen peroxide on a cerous salt), is also readily soluble in hydrochloric acid.

When the colloidal solution is treated with hydrogen peroxide or hydrogen peroxide and ammonia, it gives a yellowish red precipitate, different however from the hydrated trioxide. It turns yellowish white in color when treated with concentrated hydrochloric acid.

A portion of the colloidal solution was precipitated with sodium chloride. The precipitate was washed, boiled with concentrated hydrochloric acid and filtered. There was a yellowish white residue. It turned yellow when heated with hydrogen peroxide, or with ammonia and hydrogen peroxide, while hydrochloric acid changed it back to the yellowish white body. Evidently then the precipitate was not the hydrated trioxide.

The filtrate from the yellowish white residue mentioned in the last paragraph gave a red hydrated trioxide with ammonia and hydrogen peroxide. So then part of the reddish brown precipitate is soluble in hydrochloric acid and part is insoluble. It is evidently a mixture of oxides.

The higher oxides of cerium dissolve readily in hydrochloric acid, the lowest does not (except when freshly precipitated.) When the colloidal solution was allowed to stand for several weeks, the brownish red precipitate separated of its own accord. When the colloidal solution was placed in a dialyzer; the usual precipitate separated in about two hours. This also happened with the colloidal neodymium solution mentioned later. Mere boiling of the colloidal cerium solution caused the reddish brown precipitate to separate.

When cerous chloride solutions were electrolyzed with a stationary anode, a white preciptate of cerous hydroxide appeared. No colloid was formed. The current fell to 0.03 ampere.

A pressure of eight volts is most favorable for the formation of the colloidal solution. No colloid was produced with 3 volts or with 5 volts, but at 8 volts, the solution began to take on a pink color, showing the

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formation of the colloid. Higher voltages than 8 caused a rapid separation of the reddish brown precipitate.

With *lanthanum chloride* a current of 8 volts and 0.3 to 0.01 ampere gave at first an amalgam. There was no separation of hydroxide in the inner compartment, but the clear and filtered liquid showed a yellow tint. This colloidal solution remained stable for several weeks. Ammonium hydroxide and common salt produced white precipitates when introduced into it.

An amalgam also appeared on electrolyzing a solution of *neodymium chloride*. The liquid gradually became opalescent and in the course of a few days it acquired a deep purplish color. A solution of salt produced a white precipitate. The current employed in this experiment varied from 0.10 to 0.02 ampere.

Praseodymium chloride behaved like the neodymium salt. The colloidal solution showed slight opalescence with a brownish tint. It gave a white precipitate with common salt

In the case of *yttrium chloride* a rather stiff amalgam was formed at first, then a white hydroxide appeared, but on filtering it out the filtrate, slightly opalescent in appearance, gave a very distinct precipitate on the addition of a common salt solution. The yttrium colloidal solution is very stable.

When *ferric chloride* is electrolyzed in an ordinary mercury cup, using toluene to absorb or remove the chlorine a determination of the iron may be very accurately made. Ferric chloride, in the cell used with the preceding chlorides, exposed to the action of 8 volts and 0.8 to 0.04 ampere, became almost colorless and dark blotches appeared on the surface of the mercury cathode during which period the solution acquired a more intense brownish yellow color than at first. Quite a little precipitate separated. The filtrate from it, however, showed a brown color and when treated with sodium chloride gave a reddish brown precipitate, resembling ferric hydroxide. The colloidal solution suffered no change upon standing for several weeks. It gave no coloration on the addition of potassium sulphocyanide. If, however, the precipitate, thrown out of the colloidal solution by salt, was dissolved in hydrochloric acid and sulphocyanide added to this solution, blood red colored ferric sulphocyanide appeared. The colloidal solution could not then have contained ferric ions.

Further, when the colloidal solution was digested with hydrochloric acid and potassium iodide, iodine was liberated.

The electrolysis of a solution of *aluminium chloride* gave a gelatinous precipitate almost immediately. The filtrate from it was slightly opalescent and continued stable for several weeks. Sodium chloride produced a precipitate, soluble in sodium hydroxide.

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The electrolysis of a solution of *chromium chloride* gave a green precipitate. The solution from the latter showed no chromium. When the current of 0.9 ampere and 5 volts had fallen to 0.05 ampere a colloidal body seemed to form, because on filtering out the precipitate at this point there remained a solution green in color from which common salt precipitated chromium hydroxide. If the current was allowed to fall to 0.03 ampere, and the precipitate was then removed, its filtrate did not show the presence of chromium.

These represent our experiences in electrolyzing the chlorides of sesquioxides.

Turning for a moment to *chlorides of protoxides* it may be noted that if cobaltous chloride yields a colloidal hydroxide it is very unstable. Colloidal bodies were not observed with manganese and glucinum. In the case of cadmium chloride, the hydroxide of the metal alone was produced. Stannous chloride gave, at first an amalgam, with the separation of some hydroxide, but on filtering this out, the filtrate while clear, was brown in color and gave a brown precipitate upon the addition of a salt solution. Ammonium hydroxide was without effect. The colloidal solution became darker in color on heating, separating eventually a dark precipitate. The solution showed no reducing action with potassium permanganate. Iodine did not separate when it was treated with hydrochloric acid and potassium iodide.

Colloidal solutions were not obtained with zinc, nickel or copper. The chloride of the latter gives at first white cuprous chloride.

Stannic chloride gave an abundance of stannic hydroxide almost immediately. There was no evidence of colloidal formation. There seemed to be a slight colloidal production with *thorium chloride*, but it soon separated from its solution, while with *zirconium* and *titanium* there was complete absence of anything like a colloidal state. *Uranium chloride* gave rise to an unstable colloidal hydroxide from which uranic hydroxide soon separated.

It may then be concluded that in electrolyzing metallic chlorides as outlined in the preceding paragraphs, stable colloidal hydroxide solutions will be found with those of the sesquioxide type, while with chlorides of the dioxide and protoxide types such formation will not arise, or if it does, it will be extremely unstable.

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NOTES ON VOLUMETRIC DETERMINATION OF MAGNESIUM IN WATER.

BY G. B. FRANKFORTER AN LILLIAN COHEN.

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A rapid method for the determination of magnesium in water must necessarily be of great importance to the water analyst. The writers,

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while in search for a satisfactory method, were led to try the arsenic method as given by Stolba (Chem. Centr. 1876, p. 727). It was soon found, however, that this method was hardly a satisfactory method for water analysis on account of the difficulty of obtaining concordant results and on account of the difficulty experienced in carefully washing the ammonium magnesium arsenate. After a number of trials without obtaining satisfactory results, and in fact without reducing the time required materially over the old phosphate method, we were led to try the modified arsenic method as mentioned by R. K. Meade. In following out this method (J. Am. Chem. Soc., 1899, 746 ; Chem. News, 1899, 275-8; Sutton's Volumetric Analysis), difficulties were soon encountered, as the results obtained did not check with gravimetric results. On looking more carefully into the matter, it was found that a mistake had been made in the calculations of the original paper, and copied in the Chemical News and in Sutton's Volumetric Analysis. A glance at these calculations will show that magnesium and not oxide of magnesium is intended. As stated by Meade, arsenic acid was titrated with standard iodine solution prepared by dissolving 52.24 g. of pure resublimed iodine in a solution of 75 g. of potassium iodide in 200 cc. of water, and the whole diluted to 1 l. It was further stated that each cc. of this solution should be equivalent to 0.005 g. of magnesium oxide, according to the equation:

$$I_2 = MgO.$$

It will be seen that according to this equation the proportional weights will be as follows :

$$253.94 \cdot 40.36 :: \frac{52.24}{1000} : X.$$

Therefore, X is equivalent to 0.0082 g. of MgO and not to 0.005. On the contrary, if we substitute the atomic weight of magnesium instead of the molecular weight of magnesium oxide, we get the following :

$$253 : 94 : 24.36 :: \frac{52.24}{1000} : X.$$

X in this equation is equivalent to 0.005 g. of magnesium, which was unquestionably intended in Meade's calculation.

Having made corrections for this error, a number of determinations were made, but with only a moderate degree of satisfaction and accuracy. The chief difficulty was experienced with the starch indicator. This difficulty is apparently caused by the action of the strong hydrochloric acid on the starch solution. The acid seems to hydrolyze the starch so that instead of obtaining a blue starch iodide, a brownish color is formed which apparently does not disappear until long after the free iodine has been used up, thus resulting in a very unsatisfactory endpoint. We were unable in the presence of the stated amount of hydrochloric acid to obtain a good characteristic blue starch iodide.

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After numerous attempts to use starch as an indicator, we were led to try the titration without the use of starch, and were surprised to find a very much sharper end-point than by using the starch paste. The last drop of thio-sulphate solution changes the straw-colored solution to a perfectly colorless one, with wonderful accuracy, so that all the determinations which have been made and which appear in this paper, have been made by titration without using starch. After making a number of determinations, we were led to modify the manipulation somewhat, believing that the method is improved by this modification, especially in the determination of magnesium in water. We would recommend the following as giving best results.

Measure out 500 cc. of water to be examined, precipitate out the iron group, and calcium by the ordinary methods. Acidify and evaporate until the salts start to crystallize out. Make up to 100 cc., transfer to an Erlenmeyer flask, add one-third of the volume of concentrated ammonia and 25 cc. of a 10 per cent. solution of sodium arsenate, cork and shake vigorously for ten minutes.

The matter of precipitation during the first determination was carefully studied. A number of experiments indicated that vigorously shaking for 2 minutes is sufficient to precipitate all of the magnesium. Exactly the same results were obtained by shaking 2 minutes, and by allowing to stand before filtering, for 12 hours. After the precipitate has settled, filter and wash with dilute ammonia until the washings are free from arsenic, using as small a quantity of ammonia as possible. Now dissolve the precipitate in 50 cc. of dilute sulphuric acid (1 to 4), and allow it to run into the flask in which the precipitation was made. Wash the filter paper with hot water until the total solution measures about 100 cc. Now add 10 cc. of sulphuric acid (1 to 1), cool and add from 3-5 g. of pure potassium iodide. Allow the solution to stand for 5 minutes, and titrate with thiosulphate to straw color. Then add cautiously drop by drop, until the yellow solution becomes colorless. From the amount of thiosulphate solution used, the per cent. of magnesium may be immediately calculated.

The following analyses give comparative results of the gravimetric, of Stolba and of the Meade methods:

Sample No.		Gravimetric.	Stolba.	Volumetric.
1.	Mg—Parts per million.....	58.	66.	60.
2.	" " "	57.22	62.	58.9
3.	" " "	55.5	60.	58.1
4.	" " "	91.	96.	92.1
5.	" " "	90.4	94.	92.
6.	" " "	90.	94.	91.
7.	" " "	154.6	168.	160.
8.	" " "	153.	169.	166.
9.	" " "	160.1	170.	162.

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It will be seen that the results obtained by the volumetric method coincide very well with those obtained by the gravimetric method. It will therefore appear that this method is perfectly safe to use for rapid accurate work.

Note.—Owing to a number of errors in bibliography, the following corrections are given below:

Stolba, Zur quantitativen Bestimmung der Magnesia, Phosphor und Arsen durch Alkalimetrie. Chem. Zentr., 1876, 727 instead of 1866.

R. K. Meade, A New Volumetric Method for Magnesium. J. Am. Chem. Soc., 1899, p. 146, instead of 1889. (See Sutton's Volumetric Analysis).

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THE DETERMINATION OF CHLORIDES OR BROMIDES IN THE PRESENCE OF SULPHOCYANATES.[1]

BY M. A. ROSANOFF AND ARTHUR E. HILL.

Received July 26, 1907.

§ I. Introductory.

In the course of a research undertaken in this laboratory it became necessary to analyze a number of solutions containing mixtures of chlorides and sulphocyanates. Investigation of the literature of the subject showed that no method exists by which such mixtures can be analyzed quickly and accurately; it was found that those methods which can be relied upon for accuracy of results require such expenditure of time as prohibits their use where large numbers of analyses must be performed. In like manner search revealed no suitable method for the analysis of bromide-sulphocyanate mixtures.

To remedy this lack, the following volumetric method is proposed. It permits of an accuracy within the limits of the usual errors of measurement with pipettes and burettes, and requires less time than any of the existing methods; a single complete determination has been found to require about one and one-half hours, while two determinations can be performed without difficulty in two hours. By proper organization of the work eight to ten analyses can easily be made within a working day.

The sum of chloride and sulphocyanate, or of bromide and sulphocyanate, is established by precipitation with excess of standardized silver nitrate and determination of the excess by titration with standardized ammonium sulphocyanate, according to the method of Volhard.[2] Precipitates containing silver chloride must be filtered off before the excess of silver nitrate is determined, while in the case of the bromide filtration is unnecessary.[3] The new method has for its object, the determination of the chloride or bromide in a fresh sample of the solution, by oxidizing

[1] Presented before the New York Section of the Am. Chem. Soc., May 10, 1907.

[2] J pr. Chem., 9, 217 (1874): Z. anal. Chem., 13, 171, (1874).

[3] Rosanoff and Hill. This Journal, 29, 269, (1907): Chem. Zentr., 1907, I, 1596.

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the sulphocyanate to hydrocyanic acid by means of nitric acid, expelling nearly all the hydrocyanic acid, and determining the residual chloride or bromide, in the presence of the traces of cyanide, by the Volhard method. The sulphocyanate originally present is found by difference.

§ 2. Determination of Chlorides.

The following solutions are required: (*a*) a fifteenth-hormal solution of silver nitrate, standardized gravimetrically or by weight of silver nitrate used; (*b*) a fifteenth-normal solution of ammonium sulphocyanate, standardized against the silver nitrate by Volhard's method; (*c*) a saturated solution of iron-ammonium alum, free from chlorides and treated with nitric acid to lighten the color.

A measured volume of the chloride-sulphocyanate mixture is diluted so that the normality of the chloride is about one-fiftieth. The solution is treated with 1 cc. of the iron-ammonium alum and brought to a boil in a large Erlenmeyer flask. To the gently boiling solution concentrated nitric acid is added at the rate of about three drops a minute, during which operation the liquid should be frequently stirred to prevent superebullition. The addition of the acid in the above described manner is continued until the color of the solution has faded to a *pale orange*, and then without further addition of acid the solution is allowed to boil for a few minutes longer, by which treatment the last traces of sulphocyanate are oxidized. The complete oxidation requires about twenty minutes time; a change of color to pure yellow indicates the completion of the operation. The odor of hydrocyanic acid is now practically gone.

Cool the solution thoroughly under the tap and add to it one-third its volume of concentrated nitric acid. Add a measured amount of N/15 silver nitrate in moderate excess above the quantity required to precipitate the chloride and shake the mixture until the precipitate is well coagulated, which requires but a few minutes' agitation when the solution is cool, but *a much longer time if the solution is heated.* When the precipitate is well coagulated bring the solution again to a gentle boil, maintaining it at this temperature for about five minutes. The liquid above the precipitate must become perfectly clear.

Filter the solution while still hot through a rapid-running double filter, paying no attention to the opalescence which forms in the filtrate upon cooling. Wash the precipitate with hot water containing a few drops of nitric acid. Allow the liquid to cool thoroughly, dilute until the volume is about three times that of the solution before filtration, add 2 cc. of the iron indicator for every 100 cc. of solution and run in the standardized sulphocyanate to a strong red color. Stir the solution for five minutes and then add the standardized silver nitrate drop by drop, with stirring, until

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the color just disappears. A single drop of the sulphocyanate solution should then give a permanent pink color; should it fail to do so, titrate back and forth with the silver nitrate and ammonium sulphocyanate until the color changes on addition of a single drop. The titration is best conducted in a porcelain dish, against the white ground of which the end-point is most accurately determined; in glassware transmitted light effects may be misleading. The total silver nitrate added, *minus* the total ammonium sulphocyanate added, is the silver nitrate equivalent of the chloride present.

The following is a list of ten consecutive analyses of mixtures of potassium chloride and sulphocyanate performed according to the foregoing directions:

	N/15 KCl solution in cc.	N/15 KCNS solution in cc.	$AgNO_3$ equivalent of KCl taken	$AgNO_3$ equivalent found	Absolute error in cc.
1.	0.00	25.00	0.00	0.02	+0.02
2.	10.00	90.00	9.95	9.96	+0.01
3.	25.00	50.00	24.87	24.87	±0.00
4.	25.00	50.00	24.87	24.86	—0.01
5.	25.00	25.00	24.87	24.88	+0.01
6.	25.00	25.00	24.87	24.93	+0.06
7.	25.00	10.00	24.87	24.83	—0.04
8.	25.00	5.00	24.87	24.90	+0.03
9.	25.00	3.00	24.87	24.84	—0.03
10.	25.00	0.15	24.87	24.90	+0.03

§ 3. Determination of Bromides.

The analysis of bromide-sulphocyanate mixtures is conducted precisely as that of the chloride mixtures, with three moeifications: (*a*) the solution to be treated with nitric acid for the destruction of the sulphocyanates should be diluted to roughly one-hundredth normality with respect to bromides; (*b*) after the sulphocyanate has been decomposed at the boiling temperature and the liquid thoroughly cooled, only one-sixth its volume of concentrated nitric acid is added; (*c*) the precipitated silver salts should not be filtered off before the excess silver nitrate is determined.

The following analyses of bromide-sulphocyanate mixtures were made according to the above directions:

	N/15 KBr solution in cc.	N/15 KCNS solution in cc.	$AgNO_3$ equivalent of KBr taken	$AgNO_3$ equivalent found	Absolute error in cc.
1.	25.00	0.15	22.72	22.76	+0.04
2.	25.00	0.15	22.72	22.69	—0.03
3.	25.00	3.00	22.72	22.73	+0.01
4.	25.00	5.00	22.72	22.78	+0.06
5.	25.00	10.00	22.72	22.69	—0.03
6.	25.00	10.00	22.72	22.68	—0.04
7.	25.00	25.00	22.72	22.73	+0.01
8.	25.00	50.00	22.72	22.74	+0.02
9.	25.00	100.00	22.72	22.72	±0.00
10.	10.00	90.00	9.09	9.12	+0.03

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§ 4. Theory of the Method.

While the best test of a method is in its practical results, it is well to establish clearly the facts upon which it is based. Our method depends upon the following assumptions: (1) that sulphocyanates may be decomposed at a temperature of about 100° by such concentrations of nitric acid as are insufficient either to oxidize chlorides or bromides or to cause the volatilization of hydrochloric or hydrobromic acid; (2) that all but traces of the hydrocyanic acid formed by this decomposition can be volatilized during the time required for the oxidation itself; (3) that the silver cyanide formed by addition of silver nitrate to this solution is sufficiently soluble in hot nitric acid to be separated quantitatively from the insoluble silver chloride by filtration; and finally, (4) that small amounts of silver cyanide do not interfere with the determination of the excess of silver by means of a sulphocyanate titration, since it acts as a soluble silver salt. Each of these assumptions has been subjected to experimental investigation.

The quantity of concentrated nitric acid used during the oxidation ordinarily amounts to 2 cc. or less. If acid should be added more rapidly than the decomposition of the sulphocyanate required, there can be present at any time not more than this small amount of acid in solutions the volume of which is usually about 200 cc. Experiments were therefore conducted to ascertain whether this amount of nitric acid could be used without loss of chlorine or bromine from solutions of the concentration used in our analytical method. 200 cc. samples of N/50 chloride solution, or N/100 bromide solution, were boiled gently for fifteen to twenty minutes with varying amounts of concentrated nitric acid, and the distillates, amounting in each case to about 15 cc., were carefully tested for the presence of the halogens. The experiments tabulated below were performed in duplicate:

N/50 KCl in cc.	Conc. HNO_3 in cc.	Vol. of distillate in cc.	Cl present.
200	1.00	15	None
200	2.00	15	None
200	3.00	15	None
200	4.00	15	None
200	6.00	15	Traces
N/100 KBr in cc.	**Conc. HNO_3 in cc.**	**Vol. of distillate in cc.**	**Br present.**
200	1.00	15	None
200	2.00	15	None
200	3.00	15	None
200	3.50	15	Traces

The results show that under the conditions of analysis, loss of halogen cannot be caused by the addition of nitric acid and boiling.

The principal, but by no means the only, decomposition product of sulphocyanic acid is hydrocyanic acid. Tests showed that when a pure sulphocyanate is decomposed in the manner described, only traces of

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hydrocyanic acid remain in the solution; when the decomposition is carried out in the presence of a chloride, amounts are retained corresponding to less than two milligrams of silver cyanide. This rapid loss of hydrocyanic acid during twenty minutes' treatment appeared somewhat surprising in the light of Richards and Singer's[1] observation that the presence of chlorides prevents the expulsion of hydrocyanic acid to a marked extent. It occurred to us therefore that the decomposition of the sulphocyanate might possibly result in the formation of cyanogen rather than hydrocyanic acid, as was suggested by Knüpffer[2], who oxidized the sulphocyanate with acid potassium iodate. Accordingly, the decomposition products were passed through a solution of potassium hydroxide and the alkaline liquid analyzed; it was found to contain cyanide but no cyanate, showing the absence of cyanogen and indicating that we had in reality to do with a very rapid expulsion of hydrocyanic acid. Richards and Singer[3] expressed the view that the retention of the hydrocyanic acid by chlorides might be due to the formation of ionic complexes. Assuming this interpretation to be correct, it would appear that the complex requires a measurable time interval for its formation, and that boiling will expel hydrocyanic acid from chloride mixtures much more rapidly at the time of its formation than after the solution has been allowed to stand. It would in all probability, be a lengthy operation to volatilize the acid quantitatively, but this is unnecessary in connection with our method.

The solubility of silver cyanide in nitric acid of moderate strength, which is taken advantage of in our method of analysis, was noted by Gregor[4], who showed the marked solubility of the cyanide in 6—10 per cent. acid. In hot solutions of 25 per cent. strength we find its solubility much greater; at 80° about 0.5 cc. of N/15 potassium cyanide and 0.5 cc. of N/15 silver nitrate, corresponding to about 4 mg. of silver cyanide, can be added to 200 cc. of the acid without causing any turbidity. The amount of hydrocyanic acid left in the solution in our method is considerably less than the equivalent of this quantity of cyanide, and there is therefore no interference with the quantitative separation of the silver chloride from the decompositon products of the sulphocyanate by filtration of a hot nitric acid solution of 25 per cent. strength.

That small amounts of silver cyanide can be left in the filtrate without interference with the determination of the total silver by means of a sulphocyanate titration might be expected from the fact that in acid solution silver cyanide is much more soluble than silver sulphocyanate. Con-

[1] Am. Ch. J., **27**, 208 (1902).
[2] Z. physik. Chem., **26**, 264 (1898).
[3] Loc. cit.
[4] Z. anal. Chem., **33**, 33 (1894).

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sequently the ammonium sulphocyanate added in the titration will decompose the silver cyanide in the sense of the equation:

$$NH_4CNS + AgCN = AgCNS + NH_4CN,$$

and it will not be until the ammonium cyanide reaches a considerable concentration that the reverse action will become appreciable. To ascertain how great the concentration of cyanide might safely be allowed to become, the following experiments were conducted; a silver nitrate solution of about N/15 strength was standardized against an ammonium sulphocyanate solution, and to 15 cc. samples of the silver solution varying quantities of a N/15 potassium cyanide solution were added. In the presence of ferric iron as indicator, sulphocyanate was run into the solution until a strong red color was obtained, the mixture was stirred briskly for five minutes to afford time for the decomposition of the silver cyanide, and then silver nitrate was run in drop by drop, with stirring, to the disappearance of color. One drop more of the sulphocyanate gave in each case a permanent coloration. The quantity of sulphocyanate required for the total silver was then compared with the quantity as calculated from the original standardization of the two solutions. The tabulated results show the variation in cubic centimeters from the true titre of the solutions, the experiment being performed four times for each concentration of potassium cyanide used.

N/15 KCN taken in cc.	Extreme errors, in cc. of N/15 NH_4CNS.
0.10	— 0.01 to — 0.04
0.20	— 0.01 to — 0.06
0.30	+ 0.03 to — 0.03
0.40	+ 0.05 to — 0.01
0.50	+ 0.13 to + 0.09
1.00	+ 0.52 to + 0.12

The results show that quantities as great as 0.4 cc. of N/15 potassium cyanide solution do not affect the accuracy of the titration by amounts larger than the errors of measurement, while larger quantities cause perceptible errors in determining the true end-point. In the analytical method proposed, the amount of cyanide left in the solution is much less than half of this maximum amount.

Experiment thus substantiates the correctness of the assumptions involved in our method.

§ 5. Discussion of Existing Methods.

A number of methods have been proposed for the analysis of mixtures of sulphocyanates and chlorides. The time-consuming method of Gondoin[1], depending upon the precipitation and weighing of cuprous sulphocyanate, and that of Alt[2], depending upon the oxidation of the sulphocyanate to sulphuric acid and its determination as barium sulphate, as

[1] Z. anal. Chem., 36, 528 (1897).
[2] Ber., 22, 3258 (1889); Z. anal. Chem., 31, 349 (1892).

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well as the method of Krug and Ebroy[1], depending upon the solubility of the salts in acetone, were not investigated.

Volhard[2] proposed a volumetric method depending on the oxidation of the sulphocyanate by standardized potassium permanganate, assuming the correctness of the equation: $NH_4CNS + 3O = NH_4CN + SO_3$. No analytical results accompany the publication of the method, which has nevertheless been incorporated in some text-books. An attempt to use this method resulted in complete failure. Taking a permanganate solution standardized against oxalic acid, and a sulphocyanate solution standardized against silver nitrate, effort was made to compare the two solutions by Volhard's method. The amount of sulphocyanate found varied from 86.2 per cent. to 93.5 per cent. of that actually present, in spite of the fact that conditions of concentration, temperature, and degree of acidity were kept as constant as possible. It was found impossible to obtain either uniformity or correctness of results. This same method has been proposed independently by Jumeau[3] and by Alt[4], the latter stating that the method is inaccurate, but erroneously ascribing the irregularities to the iron usually present in commercial sulphocyanates.

Volhard[5] also proposed decomposing the sulphocyanate by oxidation with dilute nitric acid at the temperature of the water-bath, then rendering the solution alkaline with ammonium hydroxide, evaporating to drive off the hydrocyanic acid quantitatively, and determining the chloride in the residual solution. Investigation of this method brought to our notice that, although the sulphocyanate is completely decomposed, as Volhard states, yet the subsequent treatment with alkali causes in part the re-formation of the sulphocyanate. This example of a reversible reaction becomes intelligible in the light of Stokes'[6] proof that a constant decomposition product of sulphocyanic acid is isopersulphocyanic acid, $H_2N_2C_2S_3$, which reacts with alkaline cyanides according to the equation: $H_2N_2C_2S_3 + 3KCN = 3KCNS + 2HCN$. In like manner other compounds containing sulphur in the lower stages of oxidation react with cyanides to form sulphocyanates; *e. g.* Gutmann[7] makes the reaction of thiosulphates with potassium cyanide the basis of a method for the detection of thiosulphates. It is clear therefore that any method for the analysis of the mixtures under discussion will be faulty if the solution is rendered alkaline before complete oxidation of the sulphur, which opera-

[1] J. Anal. Appl. Chem., 6, 184.

[2] Ann., 190, 1 (1878); Z. anal. Chem., 18, 291 (1879).

[3] Bull. soc. chim., [3] 9, 346 (1893).

[4] Loc. cit.

[5] Z. anal. Chem., 18, 282, (1879).

[6] This Journal, 29, 446 (1907).

[7] Z. Nahr.-Genussm., 13, 261; Chem. Zentr., 1907, I, 1152; Chem. Abstracts, 1907, 1447.

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tion was found by Treadwell[1] to require two hours when the oxidizing agent was fuming nitric acid.

Borchers[2] proposes the precipitation of chloride and sulphocyanate as their silver salts, and the determination of their sum by Volhard's method; the precipitate is then washed into a flask with a stream of concentrated nitric acid and boiled with that reagent for three-quarters of an hour to the complete decomposition of the silver sulphocyanate; the solution is diluted and filtered, and the silver determined in the filtrate. Experience showed that the long boiling with concentrated nitric acid renders the method entirely unsuited for ordinary laboratory use.

Barnes and Liddell[3] precipitate the sulphocyanate as its cuprous salt by titration with copper sulphate in the presence of a bisulphite, the end-point of the reaction being determined by a drop test with potassium ferrocyanide. The authors note that the end-point cannot be determined exactly owing, as they state, to the oxidation of the copper in the cuprous sulphocyanate and its reaction with the ferrocyanide. We were unable to devise any method for rendering the determination of the end-point more exact, and found the method of use only for approximating the correct values.

Diehl[4] also precipitates the sulphocyanate as its cuprous salt, using excess of copper sulphate and a bisulphite, filters off the precipitate, and determines the chloride in the filtrate. Noyes and Abbot[5] investigated this method, and found variations between + 0.27 per cent. and — 0.49 per cent. in the amount of chlorides found; the method can therefore not be regarded as exact. Mann[6] has proposed a substitution of hydrogen sulphide for the bisulphite as a reducing agent; his results for the chloride vary from the true figures by —0.3 per cent. to — 2.8 per cent.

Incidentally to a physico-chemical research, Knüpffer[7] proposed the oxidation of the sulphocyanate by acid potassium iodate. After boiling off the hydrocyanic acid, or cyanogen, as he believes it to be, he reduces the excess iodate with sulphur dioxide, oxidizes with a nitrite and boils again to expel the iodine completely; the chloride is determined in the residue. The figures given indicate that the method is accurate; it is made very tedious, however, by the repeated boilings necessary for quantitative expulsion of the hydrocyanic acid and the iodine.

[1] *Analytical Chem.*, Vol. II, p. 261. (New York, 1906).

[2] Z. anal. Chem., **22**, 92 (1883); Borchers' Repert. anal. Chem., **1881**, 130; Treadwell's *Anal. Chem.* II, p. 261.

[3] J. Soc. Chem. Ind., **2**, 122 (1883).

[4] Chem. Zentr., 1883, 649; Ber., **16**, 2319 (1883).

[5] Z. physik. Chem., **16**, 129 (1895)

[6] Z. anal. Chem., **28**, 668 (1889).

[7] Z. physik. Chem., **26**, 262 (1898)

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The method of Rupp and Schied[1], depending upon the oxidation of the sulphocyanate by free iodine in bicarbonate solution and titration of the unused iodine, was shown by Thiele[2] to be inaccurate, owing to the incomplete oxidation of the sulphocyanate in the half-hour's time proposed by Rupp and Schied. Thiele states that if the oxidation be continued for four hours the results are accurate; in this modified form Rupp[3] has adopted the method, and claims good results from its use. In view however of Stokes' results on the decomposition of sulphocyanates and Treadwell's statement that complete oxidation to sulphuric acid requires the most vigorous treatment with fuming nitric acid, it may be doubted whether the oxidation by iodine follows quantitatively the simple equation expressed.

NEW YORK UNIVERSITY,
July, 1907.

THE USE OF SODIUM CARBONATE AND ZINC OXIDE IN SULPHUR AND ARSENIC DETERMINATIONS.

BY W. C. EBAUGH AND C. B. SPRAGUE.

Received July 17, 1907.

A method involving the use of sodium carbonate and zinc oxide for sulphur and arsenic determinations was devised by one of us[4] some years ago, and has given uniform satisfaction in various assay offices for so long a time that an account of it should be made public.

One part of dry sodium carbonate and four parts of zinc oxide are mixed thoroughly. In the case of sulphur determinations a weighed sample of the material to be analyzed, usually one half gram, is mixed intimately with enough of the sodium carbonate-zinc oxide reagent to afford at least twice as much sodium carbonate as would be required by the sulphur, arsenic, etc., present, placed in a small porcelain dish, covered with the reagent and heated to redness in a muffle for fifteen or twenty minutes. A shorter period of heating is usually sufficient, but the time here specified is ample for all cases. The residue is then extracted with water, boiled, filtered, the filtrate made acid with hydrochloric acid, precipitated with barium chloride, and the barium sulphate treated as usual.

In an arsenic determination the substance is treated as above until the alkaline solution is filtered from the residue. This filtrate is acidified with acetic acid, precipitated with silver nitrate, boiled for a few minutes and then filtered. The precipitate of silver arsenate is washed thoroughly with hot water and then dissolved in dilute nitric acid, its silver content being determined finally by titration with ammonium or potassium sul-

[1] Ber., 35, 2191 (1902).

[2] Ber., 35, 2766 (1902).

[3] Arch. Pharm., 243, 468 (1905): This Journal, 28, 1771 (1906); J. Chem. Soc. (Abstracts) 88, 867 (1905).

[4] C. B. S.

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phocyanate in the usual way. Ferric sulphate is used as an indicator. In calculating the arsenic present use the proportion :

3 Ag : 1 As : : Weight of silver found : Weight of arsenic present.

The method has been tried successfully with various sulphides such as galenite, pyrite, arsenopyrite, chalcopyrite, sphalerite, etc.; with sulphates like gypsum and anglesite; and with metallurgical products like matte, speiss and flue dust. In the case of analyses of heavyspar the method is not superior to the ordinary fusion with an alkali. The fact that the decomposition with sodium carbonate and zinc oxide has been employed for control and umpire assays upon ores in commercial work for so long a period without objection, is evidence that the results obtained by the method are accurate.

It will be seen that the method for sulphur is a modification of the well known Eschka method, and that for arsenic, is an improvement upon Pearce's method. The advantages of the decomposition described are: (1) that the mass resulting from the heating is not fused, but can be removed readily from the dish and leached with water; (2) the ease and speed with which sulphides, sulphates, arsenates, etc., are decomposed; (3) no time-consuming subsequent evaporations are necessary; and (4) the absence of a large quantity of alkaline and other salts from the solutions in which the precipitations of barium sulphate and silver arsenate are effected.

UNIVERSITY OF UTAH,
June 5th, 1907.

THE QUANTITATIVE DETERMINATION OF CARBON BISULPHIDE IN A MIXTURE OF BENZENE AND CARBON BISULPHIDE.

BY EVERHART PERCY HARDING AND JAMES DORAN.
Received August 5, 1907.

This paper is a preliminary paper to one entitled "The Technical Determination of Carbon Bisulphide in Illuminating Gas," in which determination the carbon bisulphide was separated in the form of potassium xanthate and the carbon bisulphide in the xanthate volumetrically determined by titrating with a standard solution of cupric acetate. In order to calculate the percentage of carbon bisulphide, it is necessary to know the ratio of the copper or cupric oxide to the carbon bisulphide in the copper xanthate formed.

According to the most generally accepted formula of the xanthate formed, it is a cuprous compound with the formula $(CS.OC_2H_5S)_2Cu_2$ in which the ratio of the CuO to CS_2 is 1.0:0.9561. But Edward S. Johnson[1] found the ratio gravimetrically determined, to vary from 1.0:1.593 to 1.0:1.825, depending upon conditions under which the determination was made. Macagno[2] by a volumetric method found the ratio of CuO to CS_2 to be 1.0:1.931. Others have found a ratio varying not much from that.

[1] This Journal, 28, 1209.
[2] Chem. News, 43, 148.

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of Macagno's, indicating a relationship of $CuO:2CS_2$ and that the copper compound is more probably a cupric xanthate with the rational formula $(CS.OC_2H_5S)_2Cu$.

As the ratios found by Johnson vary so much with slight changes in conditions and differ so widely from those obtained by Macagno, it was necessary to verify either one or the other of these ratios or to establish a new and more correct one. This was done by determining the carbon bisulphide in mixtures of pure benzene and carbon bisulphide by an indirect volumetric method described below.

The quantitative determination of carbon bisulphide in crude benzene and carbon bisulphide preparations presents some difficulties and up to the present time no very satisfactory method has been devised. The principal difficulty seems to be in getting the carbon bisulphide separated in the form of a compound that is stable and quantitative under varying conditions, such as, degree of acidity, excess of precipitants, dilution of solution and quantity of precipitate.

The general principle underlying the methods[1] apparently most widely practised is the separation of the carbon bisulphide by means of absolute alcoholic potash in the form of potassium xanthate and its subsequent determination in the xanthate either gravimetrically or volumetrically. Macagno[2] was the first to suggest a volumetric method for the determination of carbon bisulphide in carbon bisulphide preparations through the medium of the xanthates. This method was also used by Nickels[3] in his work on the purification of crude benzene.

Macagno obtained the carbon bisulphide in the form of potassium xanthate and titrated the cold aqueous solution slightly acidified with acetic acid with N/10 copper sulphate, determining the end point with potassium ferrocyanide. In applying his method to preparations of known carbon bisulphide content, Macagno found the ratio of CuO to CS_2 in the copper xanthate formed to be 1.0:1.931. This method gives a ratio approximate to that found by the writers. A probable disadvantage in this method is the use of an external indicator and the obscuring of the copper ferrocyanide by the yellow copper xanthate which does not readily settle making the end point difficult to ascertain. A source of error lies in the instability of the potassium xanthate in a cold acetic acid solution unless the precipitant is added at once and in slight excess.

Nickels[4] was the first to gravimetrically determine carbon bisulphide

[1] A. Vogel, Ann. Chem. Pharm. 85, 369; A. Loir, Ibid., 87, 369; Hofmann, Ibid., 95, 293; E. A. Grete, Ber., 62, 122.

[2] Chem. News, 43, 138.

[3] Ibid., 43, 148.

[4] Ibid.

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in benzene by means of the xanthates. He weighed potassium xanthate directly[1] and converted it by means of cupric sulphate into a copper xanthate and weighed this. Sources of errors in weighing the potassium xanthate lie in its instability on exposure to the air and the impossibility of removing the alkali by washing with ether. Errors in weighing the copper xanthate arise from its instability and the impossibility of obtaining a constant weight on drying.

Edward S. Johnson[2], determined carbon disulphide in a mixture of benzene and carbon bisulphide gravimetrically by separating it in the form of potassium xanthate, precipitating this with cupric sulphate in an acetic acid solution, igniting the copper xanthate formed and weighing the residue, as cupric oxide. By this method he found the ratio of CuO to CS_2 to vary from 1.0:1.593 to 1.0:1.1:82 5.258, the variation depending, as he states, upon the quantitative relation of the xanthate formed to the alcoholic potash used, the excess of copper sulphate and the dilution of the solution at the time of precipitating the copper xanthate.

The writers of this paper tried at first, modifications of Macagno's volumetric method. The slightly ammoniacal aqueous solution of potassium xanthate was titrated cold with a standard solution of dilute copper sulphate with the purpose of determining the end point by the appearance of the ammoniacal copper blue. The end point, however, was obscured by the yellow copper xanthate, which would not readily collect. The xanthate was also slightly soluble in the ammonia solution. Petroleum ether and ethyl ether were then used, respectively, to dissolve the copper xanthate immediately upon forming, hoping thus to obtain a distinct end point, but these proved unsatisfactory, due to the slow solution of the precipitate and to the absorption of some of the solution by the ether.

The following method was then devised. It appears to give quantitative results, is easy of manipulation, rapid, and fairly short.

The process in detail is as follows: In obtaining the potassium xanthate the method as used by Johnson (see following article) was closely followed. From 0.1 to 0.17 g. of carbon bisulphide (purified by redistillation and kept in a dark place) is accurately weighed, using a small weighing tube with a tightly fitting ground glass stopper and freed from the weighing tube under the benzene in a 250 cc. flask. From 60-70 cc. of pure benzene absolutely free from carbon bisulphide are used and a variable amount of absolute alcoholic potash added, about 15 cc. for each gram of carbon bisulphide present. The solution in the flask is allowed to stand about one half hour, being frequently agitated and then extracted in a separatory funnel successively, with 30-40 cc. portions of

[1] Allen, Comm. Organ. Anal., Vol. II, Part 2, p. 180.

[2] This Journal, 28, 1209.

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cold water and 1 cc. of absolute alcoholic potash until the benzene is freed from all carbon bisulphide in the form of potassium xanthate. The water and the alcoholic extractions are diluted to 500 cc. and 200 cc. portions taken for precipitation with titration. These portions are acidified in the cold with acetic acid and a distinct excess of the standard cupric acetate immediately added. The precipitate is frequently stirred from five to ten minutes, filtered, and washed three or four times with 10-15 cc. portions of cold water to remove all cupric acetate. To the filtrate is added about 3 g. of finely pulverized potassium iodide and after standing for about three minutes the free iodine is titrated with a standard solution of sodium thiosulphate whose strength in terms of the cupric acetate is known.

The following tabulation shows the results obtained by this method in establishing the ratio of CuO to CS_2 in the copper xanthate found.

Grams CS_2 taken	Excess of Cupric Acetate	Ratio CuO : CS_2
0.09825	large	1.0 : 1.925
0.09825	moderate	1.0 : 1.926
0.09825	slight	1.0 : 1.929
0.13360	large	1.0 : 1.924
0.13360	moderate	1.0 : 1.930
0.13360	slight	1.0 : 1.931
0.16826	large	1.0 : 1.926
0.16826	moderate	1.0 : 1.925
0.16826	slight	1.0 : 1.929

Average ratio = 1.0 : 1.927

This ratio is slightly lower than that obtained by Macagno and much higher than that found by Johnson. It approaches nearest to the ratio of cupric oxide to carbon bisulphide in cupric xanthate which has the rational formula $(CS.OC_2H_5S)_2Cu$ and in which the ratio of CuO to CS. is 1.0:1.9126. This tends to strengthen the belief that the compound formed is *cupric* xanthate.

Cupric acetate in acetic acid solution is an ideal precipitant giving a better formed precipitate to handle than cupric sulphate. Precipitation except in very dilute solutions is complete in five to ten minutes. Filtration is rapid and the filtrate showed no further precipitation on standing. Three or four washings with cold water are sufficient to remove all cupric acetate from the precipitate. The determination of the excess of cupric acetate by the quantitative freeing of iodine from potassium iodide, and titrating with a standard solution of sodium thiosulphate, using a starch solution as indicator, is extremely accurate.

The sodium thiosulphate solution used was standardized both against C. P. copper foil and a known weight of pure iodine free from potassium iodide by means of a standard solution of potassium bichromate.

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A blank titration was run on the cupric acetate alone, using the same amount as was used in the precipitation. The difference in the two readings gives the sodium thiosulphate equivalent to the CuO in the copper xanthate.

CHEMICAL LABORATORY,
University of Minnesota.

THE TECHNICAL DETERMINATION OF CARBON BISULPHIDE IN ILLUMINATING GAS.

BY EVERHART PERCY HARDING AND JAMES DORAN.
Received August, 6, 1907.

No satisfactory working method for the determination of carbon bisulphide in gaseous mixtures has been found by the writers in the accessible literature.

Sutton[1] in his "Volumetric Analysis" mentions a method proposed by Gastine in which the gas is dried, the carbon bisulphide absorbed by concentrated alcoholic potash, the potassium xanthate solution acidified with acetic acid, an excess of sodium carbonate added, and the xanthate then titrated with a standard iodine solution. Sutton also mentions that the gas may be passed through an alcoholic potash solution, the carbon bisulphide absorbed as potassium xanthate, the potassium xanthate solution acidified with acetic acid and titrated with a standard solution of cupric sulphate. This reference in all probability is to Macagno's[2] method for determining carbon bisulphide in carbon bisulphide preparations.

Butterfield[3] mentions a method, probably also Macagno's method referred to above, which consists in separating the carbon bisulphide as potassium xanthate, acidifying the xanthate solution with acetic acid and titrating with standard cupric sulphate.

The triethylphosphine qualitative test appears never to have been used for a quantitative determination of carbon bisulphide.

In the above methods no mention is made of getting rid of the carbon dioxide previous to the absorption of the carbon bisulphide by the alcoholic potash. Unless this is done the potash soon becomes neutralized and ineffective, the carbon dioxide ranging from 2% to 3% and even higher in illuminating gas, depending upon the purifying efficiency of the plant. The difficulty of titrating directly the potassium xanthate in an acetic acid solution with cupric sulphate was made apparent in the preceding paper. It takes some time to precipitate the xanthate in a dilute acetic acid solution and unless the cupric sulphate is added at once, the precipitate slightly dissolves. The acetylene present in the gas might also, under certain conditions, cause serious errors in

[1] Sutton, Vol. Anal., p. 367.
[2] Chem. News 43, 138.
[3] Chemistry of Gas Manufacture, p. 175.

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the titration due to possible compounds which it might form with copper.

A volumetric method was devised by the writers which apparently overcomes these objections and which gives very good comparative results. The method, in general, consists in passing the gas through a meter in absorbing the carbon dioxide by caustic potash, then drying the gas with concentrated sulphuric acid and absorbing the carbon bisulphide in absolute alcoholic potash. The potassium xanthate solution is then acidified with acetic acid, precipitated with an excess of standard cupric acetate, the copper xanthate filtered, washed and the excess of cupric acetate in the filtrate determined iodometrically.

The method, in detail was as follows: Simultaneous duplicate determinations were made to ensure the same quality of gas. The two meters used for measuring the gas were of the water type, standardized against each other and the water thoroughly saturated with the gas. After pasing through the meter the gas was first bubbled through a wash bottle containing about 50 cc. of a caustic potash solution of sp. gr. 1.27, then through a second wash bottle containing about 30 cc. of concentrated sulphuric acid and finally through two 8-inch test tubes, each containing 20 cc. of saturated absolute alcoholic potash for absorbing the carbon bisulphide. The gas thus bubbled through a column of the absorbent 20 cm. long and the flow was regulated to a nicety by means of a glass cock inserted between the absorption tubes and a water suction pump. About two cubic feet of gas was used for each determination and passed through the meter at the rate of one-half cubic feet per hour. The potassium xanthate solution in the test tubes was transferred to a beaker, the tubes rinsed with a small amount of absolute alcoholic potash, boiled to expel the absorbed gases, cooled, distinctly acidified with acetic acid and precipitated at once with an excess of standard cupric acetate. The solution was allowed to stand from one to two hours, then filtered, and the precipitate washed three or four times with 30 cc. to 40 cc. portions of cold water to remove all cupric acetate. The excess of cupric acetate was determined by adding to the filtrate about 3 g. of finely pulverized potassium iodide, allowing to stand about three minutes and then titrating the liberated iodine with a standard solution of sodium thiosulphate, using a freshly prepared starch solution as indicator.

The sodium thiosulphate solution was standardized against C. P. copper foil and also against standard potassium bichromate, and its CS_2 value calculated by multiplying its CuO value by 1.927 (see preceding paper.)

A blank was run on the same amount of cupric acetate solution as was used in the precipitation of the xanthate, thus fixing by difference the value of the absorbed cupric acetate in terms of carbon bisulphide.

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The following results were obtained on the gas furnished by the city of Minneapolis:

	Determinations	Grains per 100 cu. ft.
April 15	1	14.13
April 15	2	14.16
April 19	1	12.30
April 19	2	12.42
April 23	1	12.68
April 23	2	12.60

CHEMICAL LABORATORY,
UNIVERSITY OF MINNESOTA.

THE PROBABLE EFFICIENCY OF ACCIDENTAL GAS EXPLOSIONS.

By AUGUSTUS H. GILL AND CHARLES R. HAYNES.

Received October 27, 1906.

The amount of literature on this phase of gas explosions is apparently very small, as we were able to find no accounts of work done or tests made; yet explosions of accidental nature can easily and do often occur, since the leakage from the gas mains and pipes is always considerable, averaging about fourteen per cent. and rarely less than seven. All that is necessary is a cavity protected so that the gas shall not escape from it too rapidly, and some method of ignition.

The object of this work was to determine what part of the energy of the gas, figured from its thermal value, shows itself in external or visible work. To imitate conditions occurring in practice, this work revealed itself by raising the weighted cover of a box. In the experiments about to be described two different shapes of boxes, cubical and prismatic, of three different sizes and two types of covers, outside and inside, were employed. They were made of wood, strongly built and provided with movable covers. Although these do not simulate accurately the conditions of practice where the hard ground forms the sides and bottom, yet if the boxes be well made with dovetailed bottoms, reinforced corners and sides well hooped with strap iron, the actual conditions are closely approached.

Description of Apparatus.

The various boxes used were cubical, of one foot, four feet and eight feet capacity, also a prismatic box four feet high and one foot square in section.

The smallest box was made of 7/8 inch whitewood and was dovetailed together very strongly. It was not hooped, yet nevertheless it stood a considerable number of explosions without injury. The other three boxes were made of $1^{3}/_{8}$ inch southern pine and were at first reinforced by wooden hoops of $1^{1}/_{2}$ inch stock dovetailed. One hoop was put on each box half way down the side. These were not strong enough and iron hoops had to be added. In the prismatic box a great deal of difficulty was experienced because of the leakage along the long side joints. This

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was remedied to a considerable extent by reinforcing the corners with triangular strips running the full height. The wood used in the boxes (Georgia pine) was not well adapted to resist the shocks to which it was subjected. It is a strong wood but is too brittle and splits too easily. A softer wood better hooped would have been as strong, and leakage could have been prevented more easily.

The gas used was Boston Illuminating Gas, of the following composition: carbon dioxide 3.4%, illuminants 8.5%, oxygen 1.1%, carbon monoxide 19.1%, methane 25.1% hydrogen 27.7% and nitrogen 16.2%. Its heating power is about 600 British thermal units. The ratio of gas to air used in all the experiments was 15 to 85. The gas was admitted by a tube which passed through a hole in one of the sides near the bottom. The air displaced by the gas escaped around the cover, but as the gas diffused pretty rapidly, an excess of ten per cent. was uniformly added, for a few explosions at the first showed that a maximum explosion was not obtained with the theoretical quantity only.

In order to insure a thorough mixing of the gas and air, each box was provided with stirrers. These consisted merely of brass rods, on the lower ends of which were riveted sheet iron discs, five or six inches in diameter, and were raised and lowered from the top after the right quantity of gas had been admitted. They passed through holes bored in the cover, and no particular provision was made to keep these holes air-tight, since the air inside had to be allowed some method of egress. The holes were bored 1/64 inch large and soon worked somewhat larger. The rods were just long enough to project above the cover, and easily slipped through when the latter rose, so their weight was not lifted.

To ignite the mixture two methods were employed. With the small box an induction coil was used—this worked very well, but considerable care was necessary in the adjustment of the wires of the secondary circuit. With the larger boxes three-ampere fuse wire on a fuse block was employed. This fuse could be blown, in the mixture by connecting with the 110-volt circuit. This made a very sure and satisfactory method of ignition.

The energy was measured by noting the maximum height to which the weighted cover rose during the explosion. To determine this the following method was used, which, although rather crude, worked very well. Two strips of hard wood about four feet long, carrying a row of small tacks an inch apart, were screwed to two opposite sides of the box. From these tacks, threads were strung across over the top of the box an inch apart near the point to which it was expected the cover would rise, and two inches apart a short distance above and below.

On the cover at the centre there was mounted a block about four inches high which carried at its top a sharpened knife blade, which, as it rose

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severed the threads in its path. This method did not give accurately the actual rise of the blade, for the threads, when they were being placed in position, could not be pulled very taut without breaking, but by putting an approximately equal tension on each, the constant distance the blade had to rise above a thread in order to sever it, was easily determined, and it was found in each case that the blade went half an inch higher; that is, half the distance to the next thread. In experiments where the rise of the cover was so slight that any error in these assumptions would be comparatively great, a light frame was fastened to the uprights over the cover, and was so constructed that the knife cut threads only six inches long, thus allowing little slack.

The greatest variation of results was caused by the use of two different kinds of covers; one an outside cover, that rested tightly on the top edges of the four sides, and the other an inside cover, one which fitted down inside so that its upper surface was flush with the top edges. The first is a much nearer approach to any probable actual condition, yet the latter case might be approximated.

For weights to regulate the height of the rise of the cover, zinc slabs were employed, weighing about thirty-five pounds apiece. On the largest box nine were used and it was on account of their thickness that the knife had to be mounted so high above the cover. A recently standarized dry meter measured the quantities of gas employed.

Experiments Made and Data Obtained.

TABLE I.

Experiments with 1 cubic foot box, inside cover. Percentage gas in mixture—15. Calorific power 600 B. T. U.

	Weights (lbs.)	Height raised (ft.)	Foot lbs.	Efficiency Per cent.
(a)	21.4	1.75	37.5	0.054
(b)	33.6	2.00	67.2	0.096
(c)	33.6	2.41	81.2	0.116
(d)	33.6	2.00	67.2	0.096
(e)	33.6	1.83	61.5	0.088
(f)	52.3	1.67	87.3	0.125
			Average	0.096

The explosions (b) to (e) inclusive were made in order to ascertain how closely various explosions would check with each other if made under approximately the same conditions. It will be seen that the variation is small, and if explosion (c), in which the cover was fitted more tightly than in the others, be rejected, the deviation from the mean is very slight indeed. It will also be observed that the efficiency increased with increase of weight raised.

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TABLE 2.

Experiments with one cubic foot box, outside cover.

Explosion	Weight (lbs.)	Rise (ft.)	Foot pounds	Efficiency Per cent.
(a)	25.1	0.17	4.3	0.006
(b)	37.3	0.17	6.3	0.009
(c)	37.3	0.13	4.8	0.007
(d)	56.5	0.08	4.5	0.007
(e)	56.5	0.13	7.3	0.010
(f)	25.1	0.17	4.3	0.006
(g)	18.6	0.33	6.1	0.009
			Average	0.008

The cubical box of four cubic feet capacity was next experimented with. In the first explosions made, the cover was warped sufficiently to cause excessive leakage, but after being straightened by heavy cleats, the following data were obtained.

TABLE 3.

Four foot cubical box, inside cover.

Explosion	Weight lbs	Rise ft.	Foot pounds	Efficiency Per cent.
(a)	69.4	3.00	208	0.074
(b)	139.4	2.75	383	0.137
(c)	139.4	2.33	325	0.117
(d)	139.4	2.50	349	0.125
(e)	175.0	2.83	495	0.177
(f)	83.0	3.33	276	0.100
(g)	103.0	3.00	309	0.110
(h)	227.0	1.50	341	0.122
(i)	259.0	1.83	474	0.169
(j)	227.0	1.25	284	0.124
			Average	0.125

It will be seen with this box, as with the one cubic foot one under similar conditions, an increase of the weight to be lifted tended to increase the efficiency. Explosion (e) weakened the box at all the joints so that it had to be repaired and strengthened. It was largely owing to the excellence of these repairs that the high efficiencies obtained in the three last explosions were obtained.

TABLE 4.

Four foot cubical box, outside cover.

Explosion	Weight lbs	Rise (ft)	Foot lbs	Efficiency Per cent.
(a)	88	0.17	15.0	0.0053
(b)	18	0.29	5.2	0.0020
(c)	88	0.16	14.1	0.0050
(d)	158	0.25	39.5	0.0141
(e)	218	0.19	41.5	0.0146
			Average	0.0081

The cover used did not fit the box very closely and corrugated rubber strips were fastened to the cover to make the joints more nearly air-tight.

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A considerable weight however was necessary to produce this condition, and thus the poor efficiency of the lightly loaded cover can be accounted for.

The next set of experiments were made with the prismatic four foot box. The particular object in the experiments with this box was to determine whether or not the position of the igniting flame caused any variation in the efficiency.

TABLE 5.

Four foot prismatic box, inside, (but poorly fitting) cover.

Distance of igniting flame from top	Weight lbs.	Height feet	Foot lbs.	Efficiency Per cent.
One foot	103	0.33	34.0	0.012
One foot	103	0.42	43.3	0.015
Two feet	103	0.33	34.0	0.012
Three feet	103	0.33	34.0	0.012
			Average	0.013

The cover was about an eighth of an inch small in each dimension and the results have little value except that they show how seriously a poorly fitting cover impairs the efficiency.

TABLE 6.

Four foot prismatic box, well fitting inside cover.

Distance of igniting flame from top of box	Weight lbs	Rise feet	Foot lbs.	Efficiency Per cent.	Average
One foot	148	0.58	86.	0.031	
One foot	148	0.50	74.	0.026	0.028
Two feet	148	0.75	111.	0.040	
Two feet	148	0.83	123.	0.045	
Two feet	148	0.75	111.	0.040	0.042
Three feet	148	1.00	148	0.053	
Three feet	148	0.92	136	0.049	0.051

Two explosions were made with the igniting spark at the bottom of the box, which was not sufficiently strong and burst apart each time. It will readily be seen, however, that the efficiency of the explosion increases with a considerable degree of uniformity, as the fuse is lowered in the box.

If we compare the efficiency obtained here with that obtained in the cubical box we see that the maximum here is 0.051 per cent. as against 0.125 with a cubical box of the same capacity. This is probably due to the difference in the rate of combustion of the gas, being more rapid in the cubical box.

The difficulties with the eight foot box with regard to getting efficient explosions were considerably greater than with the four foot cubical box. The great amount of energy developed by the explosion made it impossible to hoop or otherwise brace the sides sufficiently to prevent a large dissipation of energy.

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TABLE 7.
Eight foot cubical box, inside cover.

Explosion	Weight lbs	Rise ft.	Foot lbs.	Efficiency Per cent.
(a)	163	2.08	340	0.061
(b)	163	2.25	366	0.065
(c)	236	2.08	492	0.088
(d)	301	1.50	452	0.081
(e)	301	1.33	400	0.072
(f)	341	1.33	454	0.082
			Average	0.075

Explosion (d) probably strained the box, and thereby some energy was lost by leakage, for at the next explosion one side of the box was blown completely off. When repaired the box was enough larger than before to make the cover very loose. After a few inefficient explosions had been made under these conditions, this difficulty was obviated by calking the spaces between the box and cover with cotton waste. This device although probably not as efficacious as joining the cover to fit would have been, at least prevented the escape of any undue amount of the mixture before explosion. Explosions (e) and (f) were made under these conditions and further work was prevented by their effect upon the box which needed a thorough overhauling for which there was not time.

Several attempts were made to get reliable data with an outside cover, but owing to the warped condition of the cover, a considerable weight had to be used, while an excessive weight was too likely to strain the box.

TABLE 8.
Eight foot cubical box, outside cover.

Weight lbs	Rise feet	Foot pounds	Efficiency Per cent.
243	.21	51.	0.0091
271	.21	56.9	.0101
		Average	0.096

It will be observed that these results are about an average between those of the four cubic foot and one cubic foot boxes, and it seems reasonable to conclude that with a moderately well fitting outside cover the efficiency will be about one one-hundredth of one per cent[1]. This value seems so incredibly low that the question immediately arises as to where the rest of the energy has gone. It is not easy to account for this. A large amount is wasted in heating the walls of the chamber, but probably most of it is dissipated into the atmosphere as the cover rises. The explosions in the prismatic box show incidentally that the gas does not burn instantaneously, and it can perhaps be considered that the cover is raised by the very first portion of the gas that burns, while the remainder escapes through the opening thus formed, and the fact that a large amount of gas can escape in that manner was shown by the poor efficiency of a cover which was loose fitting to a slight extent only.

[1] It has been calculated that the explosion in Expt. 1 should theoretically develop a pressure of 8 to 10 atmospheres; by calculating the force necessary to raise this cover two feet we find it to be 0.45 atmosphere. This would give an efficiency of about 5 per cent. (EDITOR).

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The increased efficiency obtained by igniting the mixture at the bottom of the cavity over that resulting from ignition at other points is exactly what would be expected, and the increase might have been greater, if the box could have been made more rigid at the bottom.

It will also be observed that the efficiency resulting from the use of an inside cover was about ten times that from an outside one. The increase varied considerably with the perfection of fit of the cover and also with the load, heavier loads showing increased efficiency. Unfortunately all this power could not usually be measured, as an excessive load almost invariably resulted in the rupture of the box and consequent loss of energy.

To sum up, therefore, it appears from the foregoing results that, under ordinary conditions of explosion and covering, such as might occur in practice, an efficiency of about one one-hundredth of one per cent. is all that could be expected, that this efficiency increases with the excellence of the fit of the covering, with the load on the cover, to be raised, and also seems to increase if the point of ignition be near the bottom rather than near the top of the cavity. With an inside cover which has to be raised through a distance equal to the thickness of the cover, before vent is given to the box, the efficiency is about ten times as great.

The results obtained in the foregoing paper agree well with the experience which one of us, (A. H. G.) and also a colleague, has had in a series of experiments independently carried out on the large scale. Some fifty explosions were made, using boxes buried in the earth and also with covered pits from 80 to 7000 cubic feet capacity.

MASS. INSTITUTE OF TECHNOLOGY.
Sept. 1906.

A STUDY OF THE LIGNITES OF THE NORTHWEST. PARTS I. MOISTURE AND HYGROSCOPICITY.

BY G. B. FRANKFORTER.
Received Aug. 24, 1907.

As a result of an investigation of the lignites from the west, northwest and north, the writer has reached the conclusion from experience extending over several years that in many respects they differ from bituminous coal to such an extent as to call for somewhat different methods of analysis and different interpretation of results. This seems to be largely due to the difference in composition and more especially to the large amount of moisture present. It has been found from analyses of a large number of samples ranging from the poorest to the best lignites of the country and from samples fresh from the mines to those exposed to the atmosphere for several months, that the moisture may vary from 6 to 40 per cent. and in a single instance 44.2 per cent. This variation is due partly to the condition underw hich the lignite exists in the seam and

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partly to the nature of the lignite itself. For instance, the brown lignite of North Dakota contains more moisture than the dark lignite farther west and north. The writer has never found the freshly mined lignite of Dakota to run below 30 per cent. of moisture. A sample direct from the Klondike[1] region gave only 22 per cent.

Freshly mined lignite loses moisture so rapidly that it is with the greatest difficulty that accurate determinations are made. As will be seen from data which follow, loss of moisture is so very rapid that as high as ten per cent. is frequently lost in the process of preparing the sample for analysis, unless precautions are taken. This fact is mentioned by the Committee on Coal Analyses[2] although freshly mined samples of lignite were probably not examined[3].

Loss on exposure to the air continues until an equilbrium is reached. Thoroughly dried lignite is very hygroscopic, absorbing moisture rapidly until an equilibrium is reached. This hygroscopicity is likewise characteristic of the lignites, for the increase in weight of thoroughly dried coal seems to be entirely due to water, there being only slight indications of the oxidation that is frequently observed in bituminous coals, either by drying at 104° to 107° or on standing exposed to the air after drying.

As a practical illustration of the rapid loss of moisture, a sample of lignite from Dakota left the mine, containing 39.3 per cent. of moisture. On arriving at its destination several days later, it contained 28 per cent., a loss of 11.3 per cent. during transportation. This loss of moisture continues more or less rapidly, depending upon the fineness of the coal, until from 10 to 12 per cent. is reached. At this point, it ceases to lose more unless the coal is badly "slaked," in which case the per cent. of moisture may drop to between 5 and 9 per cent. depending upon the fineness and the nature of the lignite and upon atmospheric conditions.

The Rate of Loss of Moisture on Exposure to the Air.—While the rapidity of the drying of coal is mentioned in the Report of the Committee on Coal Analysis and in the U. S. Geological Survey Reports and the importance of limited time taken in preparing samples for analysis emphasized, detailed results concerning the lignites are at the present time not complete. In this paper I have recorded some of the peculiar characteristics of the lignites, incidentally emphasizing the fact that modified methods of analysis are necessary in order to obtain the best results.

In order to compare results obtained by using different kinds of recep-

[1] The sample was thirty-four days in transportation but was packed in a close-fitting box.

[2] This Journal 22, 1119.

[3] Since this paper was written, a Report of the Coal Testing Plant of the U. S. Geological Survey Professional Paper No. 48 has been received. In this report Dr. Hillebrand gives a mass of facts along the same lines covered in this paper.

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tacles, some of these determinations were made in ground stoppered weighing bottles 50 mm. high and 25 mm. in diameter, some in regulation size crucibles and some in flat capsules. In each case the temperature and relative humidity were noted and the time taken for pulverizing was exact to the minute.

Samples of North Dakota lignite direct from the mine were pulverized requiring different lengths of time for the process, and the moisture determined in weighing bottles under exactly the same conditions. Samples in each case were put through a No. 100 sieve. The following per cents. were obtained:

Time in pulverizing	1 minute	30 minutes	1 hr.	2 hrs.
Moisture	37.61	34.22	32.43	31.42

The loss of moisture was greater during the first half hour pulverizing, than during the next hour and a half. That more data might be obtained, many determinations were made by exposing coal to the air for short periods of time and determining accurately the rate of loss. Experiments showed that for about ten minutes, the rate of loss per minute is practically constant; after that time the rate diminishes, in some samples slowly and in others quite rapidly. An examination into this fact showed that the rate of loss of moisture in lignite when exposed to air depends not upon the time of exposure alone but upon the physical conditions of the coal, whether pulverized or in lump; upon the temperature of the air, the relative humidity and upon the form of receptacles in which the coal is exposed and upon the amount of sample taken. The rate of loss was found to be greater in crucibles than in ordinary weighing bottles and greater in flat capsules than in crucibles. Samples of 100-mesh coal containing 31.17 per cent. of moisture were exposed to the atmosphere in a capsule 30 mm. in diameter and 5 mm. deep, in porcelain crucibles and in glass stoppered weighing bottles. The temperature was 25° and the relative humidity 29. The receptacles were arranged so that the sample could be protected from the air while weighing. In this, as in other experiments, as near two grams as possible was taken.

The following results were obtained:

	Bottle	Crucible	Capsule	
Loss after 1 minute exposure	0.13	0.16	0.196	per cent.
" " 2 " "	0.26	0.34	0.364	" "
" " 3 " "	0.39	0.48	0.533	" "
" " 4 " "	0.43	0.65	0.701	" "
" " 5 " "	0.57	0.78	0.860	" "
" " 6 " "	0.69	0.94	1.020	" "
" " 7 " "	0.91	1.10	1.190	" "
" " 8 " "	1.02	1.24	1.370	" "
" " 9 " "	1.15	1.38	1.568	" "
" " 10 " "	1.27	1.56	1.740	" "
" " 20 " "	2.00	2.53	2.81	" "
" " 30 " "	2.72	3.69	3.84	" "

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It will be seen that the rates of loss in these cases were very nearly constant for the first ten minutes. The loss was slightly less during the next ten minutes, gradually decreasing with time of exposure as indicated in the above tables. The variation in the results with the crucible is unquestionably due to the fact that it could not be closed perfectly during the weighing as in the case of the weighing bottles and capsules. I am, therefore, inclined to recommend weighing bottles in preference to crucibles for the accurate determination of moisture.

It is evident from the above data that widely varying results may be obtained from the same sample of lignite by varying the time of pulverizing and exposure, preparatory to analysis. In fact, even the preserving in stoppered bottles does not entirely prevent the loss of moisture. As an illustration of this fact, a sample of about one pound of lignite containing 39 per cent. of moisture was placed in a large bottle with a glass stopper and allowed to stand for nine weeks. At the end of that time an analysis showed only 31 per cent. of moisture.[1]

Many samples of different quality and from different localities have been examined. The following samples, two from Alaska mines and two from different parts of the Dakota fields have been selected as representing different grades of lignites:

No. 1. Beaver Hill, Yukon Valley, containing 11.77 per cent. moisture. Fresh from the mine, sample contained 26.8.

No. 2. Klondike, Yukon Valley, containing 10.47 per cent. moisture. Fresh from mine, sample contained 25.1.

No. 3. Kenmare, North Dakota, six weeks in air, 11.83 per cent. moisture. Fresh from mine, sample contained 37.6.

No. 4. Wilton, North Dakota, exposed for a few days, 31.16 per cent. moisture. Fresh from mine, sample contained 38.20.

The samples were dried in baths arranged with thermometers and a thermostat so that a constant temperature could be maintained. Toluene and xylene baths were likewise used in some of these experiments. Special air and hydrogen baths were constructed with asbestos and glass walls and a thermostat, so that a temperature varying within one degree could be maintained.

Loss by Drying Above 107°.—From a great number of determinations it was found that while lignite loses moisture very rapidly, a temperature of 104°-7° is apparently not sufficient to remove all of it. In the following tables the four above mentioned samples were taken. Just five minutes in each case were required to pulverize and pass through a 20-mesh sieve. Exactly 15 minutes more were taken in putting parts of the

[1] The Com. on Coal Analysis recommended a sealed fruit jar. A ground glass stopper is never air tight unless lubricated. Editor.

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same samples through a 100-mesh sieve. These samples were dried to constant weight under exactly the same conditions.

Dried 2 hrs. at

	No. 1 Fineness		No. 2 Fineness		No. 3 Fineness		No. 4 Fineness	
	No. 20	No. 100	No. 20	No. 100	No. 20	No. 100	No. 20	No. 100
104-7°	10.94	10.74	10.54	9.41	11.34	10.61	30.67	30.17
112-14	11.91	11.77	11.59	10.43	12.20	11.82	31.16	31.17
125-6	12.10	11.76	11.70	10.51	12.53	11.83	31.86	31.17
135-6	12.12	11.76	11.76	10.48	12.50	11.83	31.87	31.26
loss above 107	1.18	1.02	1.22	1.09	1.16	1.22	1.20	1.19

I have dried two hours instead of one. In only one or two cases has the second hour's drying made any difference. In each case I have dried one hour and weighed, then dried a second hour and reweighed. The per cent. of moisture in the 20-mesh was greater than in the 100-mesh samples. These results may be explained by the difference in the length of time required in pulverizing. The 100-mesh samples were exposed 15 minutes longer to the air than the 20-mesh samples. Furthermore, the 100-mesh samples lose moisture more rapidly than do the 20-mesh samples.[1]

A distinct loss in weight occurred above 107°. Over one per cent. of loss resulted in the raising of the temperature to 135° Most of the loss above 107°, however, occurred below 114, although a temperature of about 135° seemed necessary to obtain constant results. The question then arose as to what this loss represented, whether due to moisture or to some other cause.

Determinations were therefore made on the above samples by heating at a temperature of 135° in an atmosphere of hydrogen, and collecting whatever was driven off by the heat, in calcium chloride tubes. The loss in the weight of coal was compared with the gain of the weight of the calcium chloride tube. The apparatus finally adopted as giving best results consisted of an ordinary sized air bath with glass walls. The opposite glass ends were removed and replaced by asbestos cards. Holes were made in the asbestos cards and a combustion tube about 18 inches long inserted. One end of the tube was connected with a hydrogen generator arranged with proper apparatus for purifying and drying the gas. The other end was connected with a weighed calcium chloride tube. The weighed coal was placed in a boat and inserted in the tube. A slow but constant stream of hydrogen was passed through the tube. The bath was then heated to the desired temperature :

The following results were obtained with this apparatus :

	No. 1	No. 2	No. 3	No. 4
Loss by drying in				
air at 107° C	10.74	9.42	11.31	30.29
in hydrogen at 135°	11.82	10.69	12.23	31.29
Gain $CaCl_2$ Tube	11.80	10.75	12.34	31.35

[1] See Report of Coal Testing Plant at St. Louis.

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These results indicate that the loss resulting from drying above 107° is moisture. There were no indications that anything but water had been absorbed by the calcium chloride tube.

Drying in Desiccators.—As stated in the report of the Committee on Coal Analysis[1] moisture may be determined in coal when the amount is less than two per cent., by drying in desiccators over sulphuric acid. When coal contains more than two per cent. the method is not satisfactory. In order to test the method on lignites, a number of determinations were made. These verify the statement of the Committee. Samples of coal containing a known per cent. of moisture were dried for five days in a desiccator over sulphuric acid.

The following table will show results obtained:

Loss after 1 day	28.76	28.22	10.01
" " 2 "	32.69	29.01	10.21
" " 3 "	33.12	29.42	10.46
" " 4 "	33.29	29.66	10.60
" " 5 "	33.37	30.23	10 65
Total moisture in sample	34.81	31.65	11.60
Difference	1.44	1.32	.99

It is quite evident that drying in a desiccator over sulphuric acid is not sufficient to remove all the moisture from lignite.

Drying in Vacuum Desiccator.—Determinations of moisture were made in vacuum desiccators over sulphuric acid and under a diminished pressure of 10 mm. After practically constant results were obtained, samples were dried in an air bath at 107° and 125°, respectively.

The following table gives the loss in moisture:

	No. 1	No. 2	No. 3	No. 4
In vacuo after 1 day	10.60	10.07	11.09	30.64
2	11.01	10.34	11.51	30.84
3	11.10	10.28	11.38	30.79
4	11.10	10.31	11.51	30.84
7	11.29	10.52	11.51	30.79
Maximum	11.29	10.52	11.51	30.84
These samples were now placed in an air bath and dried.				
Dried at 107°	10.77	9.81	11.10	30.59
125°	12.10	11.10	12.39	31.41
Difference between 107° and 125° C.	1.33	1.26	1.29	0.82
Difference between vacuum and 125° C.	0.81	0.58	0.88	0.57

In these determinations the same weighing bottles and the same samples were dried *in vacuo* and in air. All the vacuum dried samples gained materially on drying in an air bath at 107° and lost by drying at 125°. The difference between the vacuum dried coal and that dried at 125° is between 0.5 and 0.8 per cent., while the difference between the

[1] This Journal, 21, 1121.

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coal at 106° and 125° is about one per cent., about the same as that obtained by drying the coal directly in an air-bath at 107° and 125°C.

In order to determine whether or not the loss and gain in the above tables were due to moisture or to oxidation, the following experiments showing loss by weight and extending over a period of eighteen months were carried out :

		No. 1	No. 2	No. 3	No. 4
Dried in vacuo over H_2SO_4	2 days	8.13	9.4	10.34	29.01
" " " " "	10 "	8.74	10.07	11.21	29.59
" " " " "	30 "	8.86	10.10	11.32	29.82
Dried in Hydrogen at 107°	2 hrs.	8.65	9.77	11.05	29.56
" " Air " "	" "	7.91	9.08	10.25	28.26
" again in Hydrogen at 107°	" "	8.67	9.71	11.11	29.22
" 1 year in desiccator over $CaCl_2$		7.01	8.05	9.25	27.28
" *in vacuo* over H_2SO_4	6 days	8.70	9.62	11.23	29.24
" in Hydrogen in Toluene bath	1 hr.	8.15	9.20	10.70	28.68
" " " " " "	5 "	8.43	9.41	10.90	29.02
" " *vacuo* over H_2SO_4	12 "	8.64	9.62	11.09	29.23
" " " " "	10 days	8.78	9.83	11.43	29.45

The maximum loss seems to have been reached after drying 30 days *in vacuo* over sulphuric acid. Drying two days longer failed to show further loss. It was expected from past experience that further loss would take place by drying at 107° in an atmosphere of hydrogen. On the contrary there was a very slight gain after drying two hours at 107°. Great care was taken in drying the hydrogen and the only explanation which seems plausible is the short exposure to the air while transferring to the hydrogen bath and while the air was being driven out of the drying oven. The increase in weight by drying the air at 107° is of special interest. In each sample the gain in weight was very marked, the samples from the extreme north gaining about one per cent., while those from the Dakota field gained about one and one-half per cent. From the peculiar hygroscopic nature of dried lignite, this gain in weight was attributed largely if not wholly, to absorption of moisture, and hence if dried again under exactly the same conditions the loss of weight ought to be the same as the previous loss. This is practically true of the first three samples. There was a slight loss in sample No. 4 by drying the second time in hydrogen.

These samples then stood one year in a desiccator over calcium chloride. The desiccator stood in a dark place and was not opened during the year. The gain in each case was very marked, being about two per cent. in each sample. Drying *in vacuo* over sulphuric acid for six hours failed to bring the loss quite back to that previously obtained by drying under the same conditions. However, after repeated drying in a hydrogen toluene bath and again drying *in vacuo* over sulphuric acid, the loss was practically the same as that obtained in the beginnig of the ex-

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periments in two of the samples. In the other two there was a slight increase in weight.

From these and numerous other experiments it would appear that no oxidation takes place in the drying of the lignite coal, but that the great variation observed in drying the lignites is due to hygroscopicity.

Hygroscopicity.—As already stated, lignite loses moisture when exposed to the air. When the sample is freshly mined the loss is so rapid as to make weighing extremely difficult in an open vessel. If exposed to the air for a long time, a point is finally reached at which the moisture may increase or decrease slightly, depending upon atmospheric conditions. If the lignite is pulverized, the loss of moisture goes on rapidly until an equilibrium is reached. The time required is about 5 days, although most of the moisture is lost during the first 2 days. Finely pulverized lignite exposed in open capsules will reach an equilibrium frequently in 24 hours. Four samples were placed in the weighing bottles, already mentioned, and weighed every day until the weights were constant.

The following table gives the results obtained :

Sample	No. 1 Beaver Hill	No. 2 Klondike	No. 3 Kenmare	No. 4 Wilton
Total moisture in sample	11.41	10.54	11.38	31.56
Per cent. of moisture lost by drying in air				
1 day	1.00	0.91	0.85	8.62
2 "	2.62	2.23	2.48	19.59
3 "	2.72	2.27	2.44	21.59
4 "	3.15	2.63	2.94	23.10
5 "	3.51	2.98	3.32	23.82
6 "	3.51	2.94	3.36	23.97
7 "	3.60	2.81	3.34	24.22
8 "	3.30	2.64	3.34	24.07
9 "	3.38	2.60	3.30	24.00
10 "	3.28	2.62	3.32	24.06
Maximum loss	3.89	3.22	4.01	24.34
Moisture in Coal after equilibrium is reached	7.52	7.32	7.50	7.22

These experiments were continued for 100 days, weighing every two days. During that time the loss never became greater than the above maximum, and never dropped more than six tenths of one per cent. below this maximum.

The above equilibria are obtained by subtracting the maximum loss of moisture from the total moisture present in the coal.

After this point of equilibrium is reached, further exposure to the air may change the equilibrium slightly, depending, however, upon the relative humidity of the air. In all these determinations the temperature and the relative humidity of the air were taken before each weighing. After the equilibrium had once been established, we were able to predict an increase or loss by weight from the temperature and relative humidity of the air. In most of these determinations the temperature was kept as

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near as possible to 22°, although during the night the minimum thermometer in the room registered as low as 18°. The relative humidity was carefully watched by means of the polymeter.

Equilibrium in Dried Coal.—Thoroughly dried lignite absorbs moisture with avidity, hence it is essential that in the ordinary determination of moisture, the dried coal should be weighed quickly or the determination should be made in closed bottles. The dried coal continues to take on moisture until an equilibrium is reached. Most of the moisture necessary to the equilibrium is absorbed in a few hours, the last trace however, is taken up very slowly. Many determinations have been made to decide whether or not the equilibrium for air-dried coal was the same as for the bath-dried coal. These determinations, while not as conclusive as they might be, owing to varying physical conditions, point, however, to the same equilibrium whether the coal is simply exposed to the air or dried in an air bath before exposure. As a result of bath-dried experiments, the following table will give the equilibria calculated as in the case of the equilibria obtained from air-dried coal:

	No. 1	No. 2	No. 3	No. 4
Total moisture in sample dried at 105-107°.	11.31	10.42	11.35	31.41
Per cent. of moisture absorbed by the dried coal after exposure of 1 day	2.53	2.06	2.24	3.63
2 "	3.72	2.84	2.75	4.07
3 "	3.65	3.14	3.50	4.12
4 "	3.80	3.16	3.70	4.09
6 "	4.30	3.69	4.09	4.43
10 "	4.88	4.70	4.63	4.07
Maximum gain	4.88	4.70	4.63	4.43

These samples were dried for two hours at 105-7°. The amounts of moisture absorbed are less than the amounts left in the samples after an equilibrium has been reached in air at the ordinary temperature. These results can not be compared unless we assume that the loss above 107° represents hygroscopic water. If we assume that the loss above 107° is due to moisture, then a comparison may be made.

The difference in loss by drying at 107° and 125° is about 1.41 per cent.

Adding this difference to the above percentages of gain by the above bath-dried samples, the following equilibria are obtained:

	No. 1	No. 2	No. 3	No. 4
Equilibrium of bath-dried lignite	6.29	6.10	6.03	5.83
" " air-dried "	6.82	6.19	6.60	6.27

Numerous experiments have been made on bath-dried samples dried at different temperatures. In each case, whether the sample had been dried at 107° or 135°, the amount of moisture absorbed after an equilibrium had been reached was from one to two per cent. less than the amount of moisture left in the samples dried in the air until an equilibrium had been reached. Samples from the Canadian Government are now under consideration.

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THE HYDROGEN OF COAL.

By Frank F Grout.

Received June 13, 1907.

Last summer, in making some calculations of the composition of coals, for the Illinois Geological Survey, working under the direction of Prof. Parr, the writer found some remarkably uniform figures for hydrogen in all coals (except anthracite and cannel[1]) and reported the same. Nothing seems to have been done with the suggestion. Some further results have been obtained since my connection with the survey has ended, and they may be of interest in connection with the recent article by Prof. Parr.[2] The facts are mentioned in Economic Geology, Vol. 2, page 231, in connection with a proposed classification of coals.

In the great number of coal analyses which have recently been published,[3] the per cent. of hydrogen in the hydrocarbon is extremely uniform. Using just such coals as those from which Prof. Parr constructs his scheme and curve, and using "pure coal" as a basis of calculation,—*i. e.*, considering the sum of carbon, oxygen, and hydrogen equal to 100 per cent.,—hydrogen is found to range only from 4.50 per cent. to 6.24 per cent. The average of some two hundred samples is 5.64 per cent., and the average error 0.30 per cent. of the pure coal. In a single coal basin, the figures are much closer. The twenty samples of Illinois coal tested, average 5.67 per cent., with an average error of 0.22 per cent.

These figures are based on a knowledge of the ultimate analyses. But if it is desired to estimate the ultimate analyses from the proximate, a different "pure coal" must be used. The proximate analysis gives us fixed carbon and volatile matter as a "pure coal" basis. This gave almost equally good figures. Using the first twenty analyses of Bull. 290, U. S. G. S, the hydrogen of the ash- and water-free coal is 5.38 per cent.; the maximum error is 0.51 per cent.; the average error, only 0.16 per cent. Now, with a carbon estimation, we have the basis of our ultimate analyses. Several instruments have recently come into the market, for a close carbon estimation, without regard to other elements present. So this work is simplified. Sulphur is usually determined, but nitrogen is still to be accounted for. This may be set down as arbitrarily as the hydrogen, but not as accurately—1.48 per cent. of pure coal. The variation noted is from 1.00 per cent. to 1.83 per cent. Now, if we subtract from the pure coal the sum of carbon and sulphur (determined) and hydrogen and nitrogen (estimated), the difference represents oxygen. The total errors which accumulate on the oxygen by these assumptions is about 1.00 per cent., as a maximum. Still, the value of

[1] These are easily distinguished by the scheme outlined in Economic Geology, 2, 225.

[2] This Journal, 29, 582.

[3] U. S. Geol. Survey, Bull. 261, 590, etc.

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such an estimated ultimate analysis is in some doubt; only, in the matter of hydrogen, it is surprisingly accurate. In comparison with other methods of determining hydrogen, the *arbitrary figure* certainly has the advantage of simplicity.

Prof. Parr offers his calculation[1] not as more accurate than that based on ultimate analyses, but if correctly understood as often giving a figure from which a close fuel value can be calculated by such formulae as Dulong's. And further, in his own words, it may "indicate other properties depending on the structure and composition of the coal." The only points emphasized are the calculation of ultimate analyses and fuel value.

The difficulty of getting a figure for hydrogen seems as great as that for determining fuel value, even if the hydrogen is calculated from the carbon percentage. One of the simplest methods of estimating carbon, is by means of the sodium peroxide combustion. But that same combustion gives the fuel value, in a simple, handy instrument, the Parr calorimeter. So what reason is there to carry the process along to a carbon estimation and complex calculation of hydrogen, only to get fuel values? These fuel values are more simply obtained by reading the thermometer of the calorimeter at one stage in the carbon estimation.

Again, assuming that one has been given the carbon estimation and not the fuel value, what method is best to use to calculate it? Prof. Parr's curve gives better results than any calculation from the proximate analysis alone. It requires a knowledge of total carbon and when this is available, another way to get the result would be to use the estimated ultimate analysis, as suggested above. If one-eighth oxygen is subtracted from hydrogen, available hydrogen is left. By the arbitrary figures given above, hydrogen seems to vary to a maximum error of 0.51 per cent., and oxygen to 1.00 per cent. Hence, available hydrogen may be in error by 0.72 per cent. The actual maximum difference between the results of this method and ultimate analysis in the coals tested was 0.44 per cent. Prof. Parr's curve gave a maximum of 0.60 per cent. The average error of this arbitrary method, from ultimate analysis, is 0.14 per cent. That for his curve is 0.20 per cent.

In calculating fuel values, it is to be noted that recent results indicate a higher value than is found by Dulong's formula and the ultimate analysis. In terms of hydrogen this would mean that as an average, 0.17 per cent. less hydrogen is found in the analysis than is required to give the fuel value actually found. By adding this amount, 0.17 per cent., to figures calculated above, one may get figures for available hydrogen, which will give good fuel values. The average error in terms of hydrogen is 0.15 per cent.; the maximum, 0.50 per cent. This seems better than any suggested calculation, and should be of practical application, especially in restricted fields. The following is a summary of the

[1] Loc. cit., p. 586.

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average errors resulting from the use of an arbitrary figure (like 5.38 per cent. as representing hydrogen in pure coal) in calculation of available hydrogen, and fuel value, compared with other methods.

H indicated by calories — H of ultimate analysis = 0.18 per cent.
H by Prof. Parr's curve — H of ultimate analysis = 0.20 "
H by Prof. Parr's curve — H indicated by calories = 0.17 "
H from arbitrary figure — H of ultimate analysis = 0.15 "
H from arbitrary figure[1] — H indicated by calories = 0.15 "

[1] Corrected 0.17 per cent., as explained in the preceding paragraph.

It is noticeable that the averages from an arbitrary simple figure are a little better than any of the more complicated ones from a curve. In view of the uniformity of these results, it is quite remarkable that the several curves and calculations that Prof. Parr has devised, did not lead even farther from the actual figures.

Summary.

In all bituminous coal, and black and brown lignite, the proximate analysis and estimation of total carbon are sufficient data for a calculation of an ultimate analysis, in which no error seems to be above 1.00 per cent., and the average, much less. The high errors are in nitrogen and oxygen, where they are of slight consequence.

The hydrogen of ash-and water-free coal is 5.38 per cent., with an average error of only about 0.16 per cent. In a limited coal field, the maximum error is undoubtedly often less than 0.51 per cent. When an arbitrary figure like this gives such close results, the uselessness of any further calculation of hydrogen is apparent.

If it is possible to obtain the carbon percentage and proximate analysis more easily than to get the fuel value, a fairly close fuel value may be calculated by Dulong's formula, and the estimated ultimate analysis suggested above. Inasmuch as recent careful work indicates that Dulong's formula and the ultimate analysis give slightly low results, it is suggested that 0.17 per cent. be added to the per cent. of available hydrogen in the ash- and water-free coal, before applying the formula. A similar correction should be applied to the estimated ultimate analysis. Then, aside from a complete ultimate analysis, this estimated ultimate analysis gives the best foundation known for calculating fuel values. But the value of such calculation seems to be confined to cases where the carbon estimation is found easier than the calorimetric work.

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THE FORMATION OF VOLATILE SULPHUR COMPOUNDS IN MEAT AND THEIR INFLUENCE ON THE DETECTION OF ADDED SULPHITES.

BY A. L. WINTON AND E. MONROE BAILEY.

Received August 12, 1907.

Sulphites are commonly detected in meat products by distillation with phosphoric acid into dilute bromine water and precipitation of the sul-

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phuric acid, formed by the oxidation of the sulphurous acid, with barium chloride. To avoid oxidation in the distilling flask the distillation may be conducted in a current of carbon dioxide or steam. The sulphurous acid is quantitatively determined by weighing the barium sulphate or by collecting the distillate in standard iodine solution and titrating with standard thiosulphate solution.

It is well known that this process, because of the oxidation to sulphate which goes on continually on exposure of the meat to the air, does not give the full amount of sulphurous acid originally added to the meat; on the other hand meat to which no sulphite has been added but which has undergone decomposition responds to the test. The latter error, if not duly considered, is liable to lead to serious injustice in the official inspection of meat products, especially in cases where samples must be sent a considerable distance in warm weather. If possible, samples should be examined while still fresh, but if decomposition has set in, only such amounts of sulphurous acid as considerably exceed that obtained by decomposition should be regarded as from added sulphites. To obtain data for use in this connection, we have conducted experiments to determine the amount of volatile sulphur compounds formed in meat and what part of this sulphur is in the form of sulphurous acid or similar combination.

The distillations were carried on in all cases in a 500 cc. flask provided with a triple-bored rubber stopper. The first hole served to introduce a stream of carbon dioxide into the liquid, the second was fitted with a funnel tube with stop-cock for the introduction of phosphoric acid, while the third carried the exit tube which in turn was connected with a vertical condenser. A 200 cc. flask served as a receiver, the distillate in all cases being passed into the bromine solution by means of a tube broadened at the lower end. Experiment proved that no sulphurous acid escaped from this receiving flask.

Determinations were first made in sodium sulphite to test the accuracy of the method of distillation. The sodium sulphite used in the experiments was ground to a fine powder and carefully mixed. As it changed considerably in composition on exposure, comparative experiments in each case were made without delay on aliquot portions of the same solution. The amounts of sulphur as sulphurous acid obtained in this material directly by titration with iodine solution and, after distillation, by the barium sulphate method follow:—

S as SO_2 By direct titration mg.	S as SO_2 By gravimetric method after distillation mg.	Error mg.
6.9.	7.1[1]	+0.2
14.4	14.2[1]	—0.2
29.3	29.0[1]	—0.3
60.9	59.6[1]	—1.3

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59.3	60.4[1]	+1.1
60.4	60.32[1]	—0.1
120.1	121.0[1]	+0.9
120.1	119.7[1]	—0.4
7.0	6.6[2]	—0.4
14.4	14.1[2]	—0.3
111.0	110.3[2]	—0.7

[1] Only water used in distilling flask.

[2] Distilled in the presence of 50 g. of fresh meat.

The following amounts of total volatile sulphur were obtained by the method described from 50 g. portions of chopped beef, mutton, veal and pork, when fresh and after standing in the laboratory for 14 days:

	Beef mg.	Mutton mg.	Veal mg.	Pork mg.
1st day	0.0	0.0	0.1	0.0
14th	1.4	2.1	4.0	2.4

In these experiments no appreciable amount of sulphur, liberated by phosphoric acid, was present in the fresh meat, but decided amounts were formed during decomposition. No attempt was made to learn the nature of these sulphur compounds. From the literature it would appear that they consist chiefly of hydrogen sulphide, ethyl sulphide, and methyl and ethyl mercaptans. Sulphites would probably be formed as intermediate products in the oxidation of sulphides to sulphates.

Search was next made for a suitable metallic salt, through a solution of which the steam from the distilling flask could be passed to precipitate hydrogen sulphide and mercaptans without affecting sulphurous acid. Sodium arsenite, lead acetate, and mercuric chloride, both in neutral and acid solutions, although removing completely hydrogen sulphide were found to hold back considerable amounts of sulphurous acid and were therefore entirely unsuited for the purpose. Dilute copper sulphate solution, (one per cent.), however, met the requirements, as it precipitated completely the hydrogen sulphide without retaining any considerable amount of sulphurous acid. The following results were obtained on aliquot portions of a solution of sodium sulphite following the usual process except that the steam from the distilling flask, before entering the condenser, was passed through 40 cc. of distilled water or of one per cent. copper sulphate. To prevent the $CuSO_4$ being carried over mechanically into the condenser during the vigorous ebullition, the exit tube was provided with a bulb and a goose neck turn.

S as SO_2 by distillation through distilled water[1] mg.	S as SO_2 by distillation through $CuSO_4$ mg.	Error mg.
8.7	8.1	—0.6
8.7	7.9	—0.8
8.7	7.9	—0.8

[1] By previous experiment it was proved that the results by distillation through water were the same as by direct titration.

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Two series of determinations of "S as SO_2" (that is of volatile sulphur not removed by copper sulphate) and of "S as H_2S" (including sulphides and mercaptans) were next made on 50 g. portions of the four principal kinds of meat in different stages of decomposition following the method outlined. At the outset the meat was chopped and the weighed portions introduced into the flasks used later for the distillation. These flasks were kept unstoppered at the room temperature and the meat allowed to decompose. The SO_2 was weighed as $BaSO_4$, the H_2S as Cu_2S. Series I is incomplete as neither qualitative nor quantitative tests for S as H_2S were made until the 9th day, whereas in series II in every case both the barium sulphate and the cupric sulphide precipitates were filtered and weighed.

VOLATILE SULPHUR COMPOUNDS FORMED BY DECOMPOSITION IN 50 GRAMS OF MEAT

SERIES I.

	Beef Sulphur as		Mutton Sulphur as		Veal Sulphur as		Pork Sulphur as	
Day	SO_2 mgs.	H_2S mgs.	SO_2 mgs.	H_2S mgs.	SO_2 mgs.	H_2S mgs.	SO_2 mgs.	H_2S mgs.
1	0.1	..	0.1	..	0.1	..	0.1	..
2	0.2	..	0.2	..	0.1	..	0.2	..
3	..	..	..	..	..	..	..	..
4	0.2	..	0.4	..	0.4	..	0.3	..
5	0.5	..	0.5	..	0.5	..	0.4	..
6	0.4	..	0.7	..	0.7	..	0.4	..
7	0.5	..	0.7	..	0.9	..	0.5	..
9	0.6	1.0	0.8	1.2	1.2	1.4	0.8	2.4
11	0.4	0.7	0.9	2.1	1.2	1.6	0.6	1.7
15	0.5	2.4	0.2	1.2	0.5	1.1	0.6	2.9
19	1.0	0.3	0.2	none	0.7	1.9	0.7	1.1
23	0.4	0.5	0.4	none	0.4	0.3	0.2	1.7
27	0.2	0.9	0.5	1.1	0.6	none	0.2	0.5

SERIES II.

	Beef Sulphur as		Mutton Sulphur as		Veal Sulphur as		Pork Sulphur as	
Day	SO_2 mgs.	H_2S mgs.	SO_2 mgs.	H_2S mgs.	SO_2 mgs.	H_2S mgs.	SO_2 mgs.	H_2S mgs.
1	none	none	0.1	none	0.1	none	0.1	none
2	0.2	none	..	..	0.1	none	..	..
3	0.2	none	0.4	0.1	0.2	none	0.2	none
4	0.1	none	0.8	none	0.5	0.4	0.1	none
5	..	..	..	..	..	..	..	..
6	0.6	none	0.5	0.2	0.5	0.5	0.2	0.5
7	0.4	1.0	1.3	0.2	0.8	0.4	0.5	none
9	0.5	0.2	2.1	0.3	1.2	3.4	0.2	1.1
11	0.2	1.0	0.5	0.2	0.8	2.8	0.4	0.6
15	0.6	1.3	1.3	0.3	0.5	2.6	0.4	0.5
18	0.1	0.2	1.0	0.2	1.9	1.8	0.2	1.2
19	..	..	..	..	..	..	..	..
23	0.2	1.1	0.2	0.7	0.5	1.5	0.2	0.8

These results, although not always uniform, show that during the first four days the S as SO_2 was in most cases inconsiderable, in only one

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case exceeding 0.5 mg., and the S as H_2S, except in the case of veal, was indeterminably small. With or without the use of $CuSO_4$ during these days there would have been no danger of declaring sulphites present when none had been added. After the 4th day somewhat larger amounts of S as SO_2 were obtained, but in no case did the amount exceed 1.9 mg. (from veal, series II).

The maximum amount of S as SO_2 obtained from beef was 1.0 mg. (series I, 19th day) and from pork 0.8 mg. (series I, 9th day). These results are especially valuable since Hamburg steak and sausages are the meat products commonly preserved with sulphites.

The amounts of S as H_2S, were larger than of S as SO_2, especially in the case of veal, the maximum being 3.4 mg. (series II, 9th day). The largest amount of total volatile sulphur was also obtained from veal, (series II, 9th day) and amounted to 4.6 mg.

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THE DETECTION OF BLEACHED FLOURS.

BY F. J. ALWAY AND R. A. GORTNER.

Received August 19, 1907.

All the processes of technical value that are used for the bleaching of wheat flour employ nitrogen peroxide as the active agent.[1] Chlorine, bromine and sulphur dioxide have been suggested, but while they bleach more or less effectively, they offer no advantages over nitrogen peroxide and possess disadvantages that the latter does not.

The results given in this article were obtained in the course of an investigation, the detailed discussion of which is published elsewhere.[2]

Early in December, 1906, paper-lined sacks were sent to twenty-four different Nebraska mills with the request that, as far as convenient, both bleached and unbleached samples of three grades of flour, *viz.*, patent, straight and bakers', be forwarded. The samples, all freshly milled, were sent by express to Lincoln. The paper linings of the sample sacks prevented sifting of the flours; accordingly the bleached flour did not enter the sacks of unbleached, while in transit. The 127 five-pound samples were placed side by side, in the order of their numbers, on the shelves of a storeroom.

Some of the mills bleach the lower grades of flour while others do not, considering that it injures the appearance of the flour. Some of the latter class, however, were so obliging as to bleach samples of their low-grade flours for the purpose of the investigation.

Besides the flours secured directly from the mills, fifteen samples, some bleached, others unbleached, that had been stored in paper boxes,

[1] Fleurent, Compt. rend., **142**, 180 (1906); Avery, This Journal, **29**, 571 (1907).

[2] Bull. 102, Nebraska Agr. Exp. Sta. (1907).

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side by side, for from two to fifteen months, were obtained from Mr. H. B. Smith, of Lincoln. A considerable number of flours obtained on the market and elsewhere, were examined, but, as the quantity of nitrites in these did not differ from those in the samples furnished by the millers, no further work was done with them.

Two unbleached flours, one a patent, and the other a straight grade, made by different mills, and of which large quantities were available, were used in bleaching experiments performed on a small scale in this laboratory. To each of these two unbleached flours there was a corresponding sample that had been bleached at the mill. In some three hundred experiments measured volumes of the bleaching agent were allowed to act upon weighed quantities of flour.

Tests for Flours Bleached by Nitrogen Peroxide.

Three changes are produced in flour by bleaching with nitrogen peroxide, *viz.*:

1. The addition of a small amount of nitrates.
2. The addition of a small amount of nitrites.
3. The change of the coloring matter of the fat or the change in the fat itself.

The tests proposed for bleached flours have been based upon one or other of the above changes. The test proposed by Fleurent[1] is based upon the change in the fat. The writers were unable to distinguish, by this test, the bleached from the unbleached flours.

Shaw[2] has proposed the use of diphenylamine sulphate, which gives an indigo-blue color with nitrates and nitrites. The method of separating the nitrates and nitrites from the flour is very tedious, and in the hands of the writers this test has failed to prove reliable.

Others[3] have used the well known Griess-Ilosvay test for nitrites and nitrous acid. The extreme delicacy of this test was pointed out by Warrington[4] in 1881. No other chemical compounds give the test and it is extremely sensitive, allowing of so small a quantity as one part of nitrite in five hundred million parts of water to be detected. It may also be employed for the quantitative determination of the nitrites in the flour.[5]

Nitrous acid and nitrites, with the Griess-Ilosvay reagent, produce a more or less intense pink coloration according to the amount present. The pink color develops within fifteen minutes at ordinary temperatures, and in less time when heat is applied to the mixture of the reagent with

[1] Compt. rend., 142, 180 (1906).
[2] This Journal, 28, 687 (1906).
[3] J. T. Willard, Bull., Kansas State Board of Health, 2, 158 (1906); E. F. Ladd, Bull., 72, N. D. Agr. Exp. Sta. (1906).
[4] J. Chem. Soc., 1881, 231.
[5] Sutton, Volumetric Analysis, p. 449.

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the solution being tested. There has been much difference of opinion as to how definitely this test distinguishes a bleached from an unbleached flour. Ladd, for instance, states that unbleached flours which have been stored beside bleached flours give the characteristic test for nitrites. Up to the present time, however, the writer has found no unbleached flour that has given even the faintest pink coloration when the test was conducted with the necessary precautions. The precautions necessary in the case of this test are extraordinary. All tests made indoors at this laboratory have proven unreliable, because the flour or the water absorbed, during the operation, sufficient nitrite, nitrous acid or nitrogen peroxide from the atmosphere to give a pink coloration with all unbleached flours. It has accordingly been found necessary to make all of the tests out of doors. Most filter papers contain small amounts of nitrites. Many natural waters as well as distilled water frequently contain considerable quantities of nitrites, those found in the latter probably being derived from the gas flames. The large amount of nitrites found in a mixture of nitrite-free water and an unbleached flour after exposure to the air of the laboratory for several hours is noteworthy.

The following method was found reliable and satisfactory both for the detection of nitrites in flour and for their quantitative determination. A laboratory table was fitted up out of doors. The water to be used in the experiments was tested in order to insure the absence of nitrites. All apparatus to be used was well washed with this nitrite-free water. The filter papers placed in funnels, were washed until the washings gave no test for nitrites. Twenty grams of the flour to be tested and 200 cc. of water were placed in a stoppered flask and shaken at frequent intervals for half an hour. The mixture was allowed to stand until the flour had largely settled to the bottom of the flask. A portion of the liquid in the flask was carefully transferred to a washed filter, and 10 cc. of the filtrate thus obtained, diluted to 50 cc. with water, treated with 2 cc. of the Griess-Ilosvay reagent, and heated in a water-bath to 80° for fifteen minutes. If no pink coloration developed, the absence of nitrites was established; if the mixture acquired a more or less pink color it was transferred to a Nessler tube and compared with a standard color solution prepared by warming a known amount of sodium nitrite with an excess of the Griess-Ilosvay reagent. Tested in this manner none of the 21 samples of flour from the eleven mills without bleachers, gave a reaction for nitrites; 46 samples of unbleached flour from 24 mills having bleachers gave none, while 12 samples sent from six of these mills as unbleached flour, gave a more or less pink color. Of the samples sent as those of bleached flours 56 gave the coloration, while two gave none. The failure of these two to give the reaction was doubtless due to the millers having sent them by mistake, as their color gave no evidence of any bleaching.

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The explanation of the coloration produced by the 12 of the samples sent us unbleached, is likewise simple; two were bleached flours, as shown both by the color and the amount of nitrites; into the others small amounts of bleached flour had been accidentally introduced. In the case of some mills the bleachers are so located that it is very difficult to take a sample of the flour before it comes into contact with the bleaching gas.

The particles of bleached flour floating in the air also add to the difficulty of getting a sample of unbleached flour. In the case of several hundred experiments in this laboratory, in which nitrite-free flours were treated with nitrogen peroxide, every sample of treated flour gave the test for nitrites.

As already pointed out it has been claimed that "unbleached flours lying along side of bleached flours, or unbleached flours from a mill where bleaching is practiced will become contaminated, as it is a well known fact that flours have the power of readily absorbing any gas or foreign odor in which they are placed."[1] If this statement were true it would not be possible to distinguish, by the Griess-Ilosvay test, between unbleached and bleached flours, in case the former had been stored near some of the latter. In the above quotation it is assumed that some of the nitrogen peroxide remains as such or as nitrous acid in the bleached flours. That the conclusions stated in the above quotation are untenable is evident from the following. Of the 58 samples of unbleached flour, from 24 mills where bleaching was practiced, only 12 gave any reaction with the Griess-Ilosvay test, the other 46 being as free of nitrites and nitrous acid as the samples of unbleached flour from mills having no bleachers. All of the samples of flour that had arrived at this experiment station previous to December 26, 1906, were tested on December 26th, to December 31st for nitrites. All were again tested on March 1st to 5th. The results of the second series of tests were the same as those of the first. During the interval of eight weeks the samples had been stored in paper-lined sacks, side by side, in the order of their numbers.

To decide whether any trace of nitrogen peroxide or of nitrous acid is given off by a strongly bleached flour the following three experiments were performed.

Experiment 1—Two beakers, the one nearly filled with bleached flour, and the other equally full of unbleached flour, were placed on a ground glass plate, covered with a bell jar and allowed to stand three days. At the end of this time the unbleached flour gave no coloration with the Griess-Ilosvay test.

Experiment 2—A layer of bleached flour, a quarter of an inch in thickness, was placed on the bottom of a Raikow gas wash-bottle and subjected

[1] Bull., 72, N. D. Agr. Exp. Sta., p. 228 (1906).

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to the action of a rapid current of air for ten days. At the end of this time quantitative determinations of the nitrites in the untreated flour and in the treated flour showed no difference in the amount of nitrites.

Experiment 3—A series of six gas wash-bottles was arranged so that a current of air supplied by a water blast passed through caustic potash solution in bottles 1 and 2, over a layer of bleached flour in bottle 3, through densely packed absorbent cotton in bottles 4 and 5 over a layer of unbleached flour in bottle 6. The flour in bottle 6 was tested every twelve hours for nitrites. At the end of forty-eight hours, no coloration being produced with the Griess-Ilosvay reagent, the experiment was discontinued. The absorbent cotton in bottles 5 and 6 was used to prevent particles of the bleached flour being carried from bottle 3. When the experiment was repeated, omitting bottles 1 and 2 from the series, the flour in the last bottle gave a distinct reaction at the end of two hours. This is to be attributed to the air of the laboratory containing nitrites, nitrous acid, or a gas which acted upon nitrates in the flour to produce nitrites; when the air was washed with caustic potash these were removed.

It is to be concluded from the above that neither nitrous acid nor nitrogen peroxide is contained in the bleached flours, the coloration with the Griess-Ilosvay reagent being due entirely to the nitrites present, and further, that an unbleached flour stored beside a bleached flour acquires none of the properties of the latter unless particles of the bleached flour are actually introduced into the unbleached flour.

The Amount of Nitrites in Flours Obtained from Nebraska Mills.

The average amount of nitrite, expressed as the sodium salt, in all the bleached samples was 6.3 parts per million of flour. There was little difference between the averages for the electrical and the chemical bleachers, they being 6.1 and 6.6, respectively. There was no general relation between the grade of flour and the amount of nitrite present. The average amounts in the three grades were: patent, 5.8; straight, 5.1; and bakers, 8.4. The largest amount found in any sample was 27.5 parts and the lowest 0.5 parts per million. It is important in this connection to note that most mills do not bleach their lowest grade for the market.

In all cases in which there was conclusive evidence that the flour had neither been treated with nitrogen peroxide nor allowed to become mixed with bleached flour no trace of nitrites was found.

Experiments With Measured Volumes of Nitrogen Peroxide.

Very little has hitherto been reported as to the effects of varying amounts of nitrogen peroxide upon a definite amount of flour. Fleurent states that the amount of nitrogenous matter added in the bleaching process varies from 20 to 50 parts per million of flour, or 18 to 38 parts

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per million of bread, and that the volume of nitrogen peroxide required to bleach one kilogram of flour varies from 15 to 40 cc.

Nitrogen peroxide, itself, cannot conveniently be measured on account of the readiness with which it is absorbed by water and other liquids, and because its relative density changes with the temperature. Nitric oxide, however, may easily be obtained pure, and may conveniently be measured over water; when it is brought into contact with the atmosphere it is entirely changed into nitrogen peroxide, provided that the volume of the air is not less than 2½ times that of the nitric oxide.

The method of bleaching flours practiced by the writers was as follows: A weighed quantity of flour, from 200 to 1000 g., was placed in a 3-liter glass flask. By means of a glass tube, drawn to a long fine point and reaching to the middle of the flask, the desired volume of nitric oxide was delivered from a gas burette. The glass tube was at once withdrawn, the flask stoppered and vigorously shaken. Before delivering the first measured portion of gas a large quantity of nitric oxide was passed through the delivery tube to expel all air. When a considerable number of samples of flour were treated in rapid succession the capillary end of the delivery tube prevented any appreciable diffusion of gas. Where the volume of nitric oxide was less than 50 cc. per kilogram of flour, the brown fumes disappeared quickly on shaking the flask. With larger proportions of gas the shaking had to be continued longer, with 100 cc. from one to two minutes and with 1000 cc. more than five minutes.

On October 16th, 1906, fifteen portions of an unbleached flour were treated with different amounts of nitric oxide, varying from 5 cc. to 1000 cc. per kilogram.

TABLE I.

THE EFFECT OF DIFFERENT QUANTITIES OF NITROGEN PEROXIDE UPON THE SAME FLOUR.

No. of Experiment	Volume of nitric oxide per kg. of flour.	Weight of nitrites per million parts of flour	Color of flour	Color of fat solution in ether	Color of solid fat
0	0cc.	0	Yellow	Yellow	Yellow
1	5cc.	——	Light yellow	Light yellow	Light yellow
2	10cc.	6.25	(1)	(1)	(1)
3	20cc.	7.50			
4	30cc.	12.50			
5	50cc.	25.00			
6	75cc.	40.00			
7	100cc.	50.00	White	Colorless	Almost colorless
8	125cc.	37.5	Whtie	Colorless	Almost colorless
9	150cc.	30.0	(1)	(1)	(1)
10	175cc.	30.			
11	200cc.	24.			
12	300cc.	15.			
13	400cc.	16.			
14	500cc.	12.5			
15	1000cc.	6.6	Light yellow	Light yellow	Brownish yellow

1. The change in color from number to number between 2 and 7 and again between 8 and 15, was too small to be satisfactorily described.

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The colors of the fifteen bleached samples were compared by Pekar's method. There was a distinct difference between the unbleached flour and that to which nitric peroxide had been applied at the rate of 5 cc. per kilogram. The difference between adjacent members of the series of bleached samples was very slight, but when samples, separated by two numbers, such as No. 3 and No. 6, were compared, a difference was apparent. There was an increase in the whiteness from No. 0 to No. 8 (125 cc. per kilogram), and a decrease from No. 8 to No. 15 (1000 cc. per kilogram). Twenty-five grams of each flour were extracted with ether. The ethereal solutions of the fats thus obtained were diluted in each case to 50 cc., and their colors compared. No. 0 was bright yellow, No. 8 colorless, and No. 15 very slightly yellow. The colors of the fat solutions bore the same relations to one another that the colors of the flours did. The solid fats were obtained by the evaporation of the ethereal solutions, and their color and odor compared. Qualitative tests made soon after the bleaching in October showed very large amounts of nitrites in Nos. 7 to 15, but the quantities had become surprisingly small before the quantitative determination was made at the end of December. Other series of experiments gave results similar to the first, the maximum bleaching effect being produced by from 100 to 150 cc. of nitric oxide per kilogram of flour; larger amounts imparted a yellow color to the flour. When the maximum bleaching effect was attained the fat was practically colorless and gave a colorless ethereal solution. The odor of the flour remained agreeable when the amount of nitrogen peroxide did not exceed this amount. The greater the amount of nitrogen peroxide that was used in excess of the quantity required for this maximum effect, the darker was the color of the flour and also of its extracted fat, the more yellow was the ethereal solution of the latter, the more disagreeable was the odor of the flour, and the more objectionable its use for bread making purposes. It is highly probable that many of the adverse opinions that have been expressed regarding bleached flour are due to the investigation of samples to which excessive quantities of nitrogen peroxide had been added, and which might be designated "overtreated" flours.

In order to decide whether it is possible from the amount of nitrites in bleached flour to estimate the amount of the bleaching agent that has been used, a large number of flours were bleached, and allowed to stand three or four weeks before the final determination of nitrites was made. The results, given in Table 2, indicate that it is possible to make an approximate estimate of the amount of nitrogen peroxide that has been used.

The amount of nitrite found in a bleached flour is approximately proportional to the amount of gas used, up to 50 cc. per kilogram; the

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TABLE 2.

THE QUANTITY OF NITRITES PRODUCED BY THE ACTION OF DIFFERENT QUANTITIES OF NITROGEN PEROXIDE UPON THE SAME WEIGHT OF FLOUR.

Experiment number	Volume of nitric oxide used for each kg. of flour	Weight of nitrites per million of flour	Series number of flour	Reported grade of flour
1	2 cc.	3.7	112	Straight
2	2 "	3.3	113	Bakers'
3	2 "	3.1	113	Bakers'
4	2 "	3.0	131	Straight
5	2 "	3.0	131	Straight
6	2 "	4.2	139	Patent
7	2 "	4.3	139	Patent
8	2 "	3.8	132	Bakers'
9	5 "	7.8	120	Patent
10	5 "	7.8	120	Patent
11	5 "	6.2	23	Bakers'
12	5 "	6.0	23	Bakers'
13	5 "	5.6	130	Patent
14	5 "	5.6	130	Patent
15	5 "	6.4	132	Bakers'
16	5 "	6.4	132	Bakers'
17	5 "	6.4	140	Straight
18	5 "	5.6	140	Straight
19	5 "	6.5	141	Bakers'
20	5 "	5.1	141	Bakers'
21	25 "	20.3	20	Bakers'
22	25 "	20.0	89	Bakers'
23	25 "	18.1	147	Patent
24	25 "	23.0	147	Patent
25	25 "	21.5	147	Patent
26	25 "	19.0	147	Patent
27	25 "	21.0	147	Patent
28	50 "	30.0	147	Patent
29	50 "	30.0	147	Patent
30	50 "	31.1	147	Patent
31	50 "	27.0	147	Patent
32	50 "	33.0	147	Patent
33	50 "	30.0	147	Patent
34	50 "	31.0	147	Patent
35	50 "	32.0	147	Patent
36	50 "	31.0	147	Patent
37	50 "	29.0	89	Bakers'
38	50 "	28.5	20	Bakers'
39	80 "	30.0	A mixture of 147 with 5%	shorts
40	90 "	43.0	A mixture of 147 with 10%	shorts
41	90 "	38	A mixture of 147 with 20%	shorts
42	100 "	26		Shorts
43	100 "	50	145	Straight
44	100 "	42	20	Bakers'
45	100 "	40	89	Bakers'
46	100 "	60	147	Patent
47	100 "	52	147	Patent
48	100 "	51	147	Patent
49	100 "	49	147	Patent
50	100 "	56	147	Patent
51	100 "	40	147	Patent
52	150 "	55	147	Patent
53	200 "	58	147	Patent
54	200 "	60	147	Patent
55	250 "	56	147	Patent
56	300 "	42	147	Patent
57	400 "	31	147	Patent
58	500 "	26	147	Patent
59	1000 "	10.0	147	Patent

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more gas that is used the smaller is the proportion of it left as nitrite in the flour, 2 cc. per kilogram giving from 3 to 4 parts per million of nitrites, and 50 cc. per kilogram giving only 30 parts per million. When not more than 50 cc. per kilogram of flour had been used the proportion of nitrites was not found to become less on allowing the flour to stand, while with the larger volumes of gas the amount of nitrites fell rapidly; the more nitric oxide that was used up to 1000 cc. per kilogram the smaller was the quantity of nitrites eventually found in the flour.

TABLE 3.

THE CHANGE IN THE AMOUNT OF NITRITES IN BLEACHED AND IN OVERTREATED FLOURS.

Experiment number	Series number of flour	Volume of nitric oxide per kg.	Date of bleaching	Nitrites per million of flour		
				March 1	March 4	March 27
22	89	25	Mar. 1	21		20
23	147	25	Feb. 28	20		18.1
24	147	25	Feb. 28	19		23
28	147	50	Feb. 28	30		30
29	147	50	Feb. 28	30		30
32	147	50	Feb. 28	30		33
35	147	50	Feb. 28	30		32
52	147	150	Feb. 28	170	80	55
53	147	200	Feb. 28	92		58
55	147	250	Feb. 28	150	92	56
56	147	300	Feb. 28	115	106	42
57	147	400	Feb. 28	155	112	31
58	147	500	Feb. 28	245	110	26
59	147	1000	Peb. 28	334	85	10

As is evident from this table the mere determination of the amount of nitrites does not serve to distinguish a flour to which an objectionably large quantity of bleaching agent has been applied, (an over-treated flour), from one to which only a comparatively small amount has been applied. This is not a serious matter, however, because a miller is not apt to overtreat a flour when, by so doing, he not only injures the quality of the flour but also, by spoiling its color and odor, lowers its market value. All overtreated flours, (produced in this laboratory), that the writers have examined have given a bluish coloration when added to diphenylamine in sulphuric acid solution. A small quantity of the overbleached was first moistened with water, and then stirred into this test solution.

The volume occupied by a definite amount of gas depends upon the temperature and pressure. As the differences in the weight of a given volume of the nitric oxide, due to the varying pressure of the atmosphere and the slight fluctuations in the temperature of the laboratory, are much smaller than those due to the method of determination, neither the temperature nor the pressure is given in the tables 1, 2 and 3.

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In order to determine how concordant the results were for the same flour, the quantity of nitrites in a mill-bleached flour was determined on each of several different days by three different persons. The results ranged from 11 to 15 parts of nitrites per million parts of flour.

The Action of Chlorine and Bromine Upon Flour.

An unbleached flour was treated with different amounts of chlorine and bromine. The maximum effect was produced by the use of approximately 0.7 g. and 1.6 g. respectively, of the bleaching agents for each kilogram of flour. When the quantity of the bleaching agent exceeded 0.8 g. in the case of bromine, or 0.35 g. in that of chlorine, for each kilogram of flour, there was an increase in the acidity of the latter. The greater the excess of the bleaching agent the more acid was the flour.

By means of the following test it is possible to detect a flour that has been bleached by chlorine or bromine even when the quantity of bleaching agent does not exceed 0.035 g. of chlorine or 0.08 g. of bromine per kilogram of flour. Thirty grams of the flour are extracted with benzene, and the latter evaporated. A small amount of oil remains. A piece of copper wire is heated in a colorless gas flame until it is black and no longer colors the flame green. The hot end of the wire is dipped into the oil and again brought into the flame. If chlorine or bromine has been used as a bleaching agent, a green or blue coloration will be produced.

It is evident from the above test that chlorine and bromine are largely absorbed by the oil of the flour. When the quantity of bleaching agent used exceeded 0.175 g. of chlorine or 0.40 g. of bromine per kilogram of flour it was possible to estimate the amount that had been used. A watery extract of the flour was prepared and titrated with decinormal silver nitrate solution. It was found that in each case practically half of the chlorine or bromine added to the flour had been left as chlorides or bromides.

Conclusions.

1. A bleached flour may with certainty be distinguished from an unbleached flour, and the kind of bleaching agent employed may be identified as nitrogen peroxide or halogen. The amount of bleaching agent that has been applied to a flour may be estimated from the amount of certain reaction products remaining in the flour.

2. With the Griess-Ilosvay reagent all flours bleached by means of nitrogen peroxide give a pink coloration, while unbleached flours give no coloration. Only when extreme precautions are observed is the test reliable.

3. Bleached flours lying along side of unbleacded flours do not give off any substance which will so effect the latter that they will give the test for bleached flours. Neither nitrogen peroxide nor nitrous acid is present in bleached flours, the characteristic reaction being produced by nitrites.

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4. The amount of nitrites in bleached flours is very small, the average being 6.3 parts per million for all the samples examined. There is little difference in the amount of nitrites produced by the two kinds of bleachers.

5. The amount of nitrite in a bleached flour is approximately proportional to the amount of nitrogen peroxide that has been used. The average amount of the bleaching agent used by twenty-five Nebraska mills would accordingly be approximately 5 cc. per kilogram of flour.

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THE COMPOSITION OF SOME EDIBLE SEEDS FROM CHINA.

BY RALPH W. LANGLEY.

Received July 31, 1907.

The chemical study of the products described in this paper was undertaken at the suggestion of Prof. Lafayette B. Mendel, to whom the seeds had been forwarded by the Hon. Wu Ting Fang, ex-Minister to the United States from China, with a request for information regarding their nutritive value.

Three types of seeds were examined

Chinese Lotus	*Nympaea tetragona*
Chinese Sweet Almond	*Prunus Amygdalus*
Gingko Nut	*Gingko biloba*

The literature on food stuffs contains few references to these plants or their seeds.

The sweet almond is reported to contain 2.9 per cent. of cane sugar and *Lotus Suaveolens* an alkaloid cytosine, $C_{11}H_{14}N_2O$.

Lotus Arabicus is stated to contain a glucoside, lotusin, associated with an enzyme, lotase.[2] Under the influence of the latter, or when boiled with a dilute mineral acid, lotusin yields glucose, prussic acid, and lotoflavin, $C_{15}H_{10}O_6$. *Gingko Biloba* also called the maidenhair tree, is fully described in the annals of Botany, XIV. It is cultivated as a sacred tree in gardens in China and Japan, and is grown to some extent in Europe and America. It sometimes attains a height of 30 meters and a circumference of 8 meters. Formic acid has been found in the growing tree,[3] and the nuts contain caprylic acid and as much as 4 per cent. cane sugar.[4]

Methods of Analysis.

Only the edible portion of the nuts were used. In the case of the gingko nuts the kernels comprise 59 per cent. and the shells 41 per cent. of the entire nut. The gingko nuts and lotus seeds were ground to a

[1] Czapek, Biochemie der Pflanzen, I, 306.
[2] Loc. cit.
[3] Ibid 2, 442.
[4] Ibid 1, 306.

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fine powder, while the almonds were sliced as fine as possible. The latter process was necessary to retain the oil which is present in abundance. Unless otherwise stated, the methods used were those of the Association of Official Agricultural Chemists.[1] Starch was determined by the diastase method in the residue after extraction with ether. In the case of the almonds, the sugars were removed by boiling with 95 per cent. alcohol and estimated as cane sugar by Allihn's method after inversion with HCl.

Moisture determinations on the air dry material gave:

	Per Cent. H_2O
Gingko nuts	15.7
Lotus seeds	12.2
Almonds	7.3

Proteids were determined by multiplying the percentage of nitrogen found by the Kjeldahl method by 6.25.

In each case the seeds were thoroughly extracted with ether and then with 95 per cent. alcohol and nitrogen determined on the residue. The same percentage of nitrogen was found before and after extraction, showing that the nitrogen present is all in a form insoluble in alcohol, at least within the limits of experimental error (0.1 per cent).

Fats were determined by extracting the dry sample with ether for twelve hours, grinding to a fine powder and extracting for twelve hours more.

In the case of the almonds, the sliced material gave 54 per cent. fat without grinding, 56.5 per cent. when coarsely ground and 57.3 per cent. when powdered.

Pentosans were determined by distilling with HCl and precipitating furfuraldehyde with phloroglucinol as described by Krober, Rimbach and Tollens.[2]

The results were calculated to "pentosans in general" using the tables in Z. physiol. Chem., **36**, 239.

Starch was determined by the diastase method, care being taken to see that no starch remained unaltered. In the case of the lotus seeds and gingko nuts, the samples were not extracted with alcohol, and any soluble sugars are included in the figures for starch.

Cane sugar was determined in the almonds by extracting with ether and boiling 95 per cent. alcohol, inverting with HCl (2 per cent.) and determining invert sugar by Allihn's method. The results are as follow and are calculated to moisture free material:

[1] Bull., **65**, Bur. Chem., Dept. Agri.

[2] Z. angew. Chemie., 1902.

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	Gingko Nuts	Lotus Seeds	Almonds
Protein (N x 6.25)	13.1	21.3	25.0
Starch	67.9	47.0	none
Fat (ether ext.)	2.9	2.6	57.3
Ash	3.4	4.5	2.7
Fiber	1.0	2.8	3.1
Pentosans	1.6	3.6	3.8
Cane Sugar	Not det.	Not det.	2.1

The iodine absorption number of the fat of the almond was 92.3 per cent. and its reading on the Zeiss butyrorefractometer 70.5° at 15.5°, its refractive index being 1.4726.

The lotus seeds were distilled with $\frac{N}{1}H_2SO_4$ and no HCN could be detected in the distillate, showing that no glucoside is present capable of forming HCN.

Analyses were made of the ash of the seeds. The material being charred below redness, extracted with dilute HCl and charred to a white ash and added to the first HCl solution.

Iron and aluminum were separated by the basic acetate method, and determined where present in sufficient amount. Calcium was determined in the filtrate in acetic acid solution. Separate portions were used for alkalies and P_2O_5.

	Gingko Nuts	Lotus Seeds	Almonds
Fe_2O_3	0.05	0.08	trace
Manganese	trace	trace	trace
CaO	1.0	6.25	10.70
MgO	7.0	9.23	13.80
P_2O_5	14.7	37.00	37.50
Na_2O	trace	0.1	trace
K_2O	55.2	36.9	34.6

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NOTE.

Determination of Crude Fiber.—Owing to the large number of crude fiber determinations required of this laboratory—1700 were made the past year—it is impossible to adhere strictly to the official method as laid down in Bulletin 46, and the following modification is used:

Weigh 2 g. of the substance in an S. and S. Hülsen capsule. Dry for four hours in water oven. Extract with ordinary ether or use the residue from the determination of the ether extract. To this residue, in a graduated 700 cc. lipped beaker, add 200 cc. of boiling, 1.25 per cent. sulphuric acid; cover the beaker with a watch glass. Boil at once and continue boiling for thirty minutes, being careful to keep the volume to

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200 cc. Filter on a Büchner funnel, using a linen filter; wash with boiling water till the washings are no longer acid; wash the substance back into the same flask with 200 cc. of a boiling, 1.25 per cent. solution of sodium hydroxide, free, or nearly so, from sodium carbonate; boil at once and continue the boiling for thirty minutes in the same manner as directed above for the treatment with acid. Filter on a glass funnel, using Hirsch's porcelain filter plate, asbestos pad one fourth inch thick, and suction. Wash six times with boiling water, once with 10 cc. glacial acetic acid (1 part acetic acid to 20 parts of water); wash again six times with boiling water and twice with 95 per cent. alcohol. Transfer asbestos pad and substance to a platinum dish; dry four hours at 110°, weigh and incinerate completely. The loss in weight is crude fiber.

To obtain concordant results it is necessary to treat the asbestos with boiling 1:2 hydrochloric acid for two or three days. Wash free from acid and digest with boiling soda solution for two or three days; wash free from soda; dry and incinerate. The asbestos may be used over and over again.

It is found convenient to rig up two seven or eight liter flasks over the filtering apparatus to hold boiling water, for washing the substances.

By following the above method, two men find no difficulty in digesting and transferring twenty-four substances in 3 1/2 hours. Checks of 0.2 per cent. are easily obtained, and generally the duplicates come closer than the above limit.

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CORRECTION.

'*The Specific Heat of Solids at Constant Volume, and the Law of Dulong and Petit.*—The paper under the foregoing title, which appeared in the August number of this Journal went to press without revision of the proof by the author, and a number of typographical errors thus crept in:

On page 1165, last line, for C_v read c_v.

On page 1166, equation (4) should read,

$$c_p - c_v = \frac{T \beta^2 v}{a}.$$

On page 1167, the equation should be numbered (5).

On page 1167, fifth line from bottom, for a read β.

On page 1168 the value of C_v for aluminum should be 5.6 and for zinc .7. The value of Δ_2 for cadmium should be 0.0 instead of 0.5. This

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misprint made it appear that cadmium deviates widely from the modified law of Dulong and Petit while it really has exactly the normal atomic heat. GILBERT N. LEWIS.

Dr. Lewis's paper has been of especial interest to me for the reason that I reached the conclusion some years ago that the real basis for the law of Dulong and Petit is the same as that for the law of Avogadro and this conclusion was presented in some of my classes. The point of view which led to this conclusion was as follows:

In accordance with the kinetic theory the law of Avogadro, depending as it does, on the law that all gases expand equally for equal increases of temperature, is based on the fact that molecules of different weight when in collision exchange energies as elastic bodies so that the value mv^2 is a constant, independent of the mass of the molecule. In other words, the velocity of a molecule varies inversely as the square of its mass, and the average energy of translation for a molecule is independent of its mass. This is exactly parallel with the law of Dulong and Petit, which is, that the energy required to raise the temperature of an atom one degree is constant and is independent of its mass. W. A. NOYES.

NEW BOOKS.

ELEMENTARY PRACTICAL CHEMISTRY. PART I—GENERAL CHEMISTRY BY FRANK CLOWES, D. SC., AND J. BERNARD COLEMAN, A. R. C. SC. LONDON—J. AND A. CHURCHILL. Price $1.00.

The writer found on reading here and there in this little volume, designed for beginners, that it gives most excellent and explicit directions for practical, elementary work in chemistry, and that the chosen experiments beautifully illustrate the principles under discussion. It is difficult to comprehend how any earnest student, using this book to acquaint himself with the fundamentals of chemistry, could fail to develop a deep interest in the science, or fail to arm himself with an abundance of necessary facts with which to proceed to more advanced work in the subject. There are, at the present time, so many admirable introductions to chemistry that it is difficult for the student to make his selection. Each book aims to set forth the views which its author considers most essential, when introducing the neophyte to the mysteries of chemistry. The present volume has its distinct ear marks in this direction, and to the writer's mind they seem to indicate a very proper course, which he hereby sympathetically endorses. EDGAR F. SMITH.

DENATURED OR INDUSTRIAL ALCOHOL. BY RUFUS FROST HERRICK. New York, John Wiley & Sons, 1907. 516 pages. Price $4.00

The recent passage of bills through congress making the long hoped-for sale of tax-free alcohol a possibility in the United States has created a need for a work giving practical details on many subjects connected with the manufacture, sale and application of denatured alcohol. The present compilation by Mr. Herrick seems to satisfy the requirements in

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such a book very satisfactorily, as it covers just such points as the manufacturer and user are most likely to be interested in.

The book deals not only with the chemical questions involved in the manufacture of common alcohol and the various denaturing agents, but includes also various other matters such as the uses of alcohol in lamps, stoves, and engines, with numerous illustrations of types of these appliances employed in this country and in Europe, the relative efficiency with respect to cost, of various fuels and illuminants, the cost of alcohol from different sources in different countries, the laws of this and other countries governing the preparation and sale of different grades of alcohol etc., etc. A book of this character is necessarily a compilation from a great number of sources, and in consequence is somewhat fragmentary. Different sections of such a book are unequally important and reliable, and this is true of the present work. While the real value of much that is presented here may be doubtful, the book as a whole must be pronounced a valuable contribution to our technical literature and will doubtless prove of value to many manufacturers who are ready to embark in new enterprises depending on the use of free alcohol.

J. H. LONG.

BEET-SUGAR MANUFACTURING AND REFINING, VOL. II, EVAPORATION, GRAINING AND FACTORY CONTROL. BY LEWIS S. WARE. First Edition. New York, John Wiley & Sons. London: Chapman & Hall, Limited. 1907, pages VI + 647. Cloth $5.00 (21/-net).

Until recently the beet-sugar technicist of the United States has had to depend entirely upon German and French treatises for instruction in the science and art of sugar production. The university man has not, in general, been attracted to this line of work, while the student from the public schools has found the whole subject a sealed book, from the fact that he was unable to read a foreign language.

For a matter of ten years the translation of some one of these texts has been eagerly looked for and some private translations exist, but have been withheld from publication.

The want is filled by the present volume, which brings the wealth of information and the pith of the knowledge contained in the leading foreign treatises, built up about the author's evident own large knowledge and experience.

The subject is one of purely physical operations, and while the writer has apparently assumed that the reader has a good general education, the style is marked by extreme simplicity and thoroughness. Credit is unhesitatingly given to the original authority, when the statement is not a matter of general knowledge, and the very numerous original references are commendable. The author frequently refers to the standard work

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of Classen, while the no less eminent experts, Horsin-Déon and Dessin, have been freely drawn upon in the treatment of multiple effect evaporation.

The main topics are, Evaporation, Manufacture of Raw Sugar, Working After-Products, Manufacture of White Sugar, Utilization of Residues, Steam Economy and Practical Working.

Under the subject of Evaporation, all those factors that make for economy in working, quality of product and lengthening the life of machinery are treated from a practical standpoint. The various approved modern forms of apparatus are described and illustrated, emphasis being placed upon their distinguishing characteristics and the latter almost invariably given special illustration. The subject of intrainment deserves particular mention. as the author explains its cause very fully, giving authoritative figures as to its extent, and goes intimately into the description of, and comment upon the many remedies applied, including the centrifugal type of catch-all. The various forms and arrangements of heating tubes are discussed, with and without devices for ruissellement.

Among the several multiple effect systems illustrated and described may be mentioned those of Cail, Rillieux, Brunswick, Wellner and Jelinek, Yaryan, Lillie, Moriolle-Pinquet and Witkowicz. The theory and practice of jet-condensers, parallel- and counter-current, under dry and moist pump systems are well illustrated and explained, including the spray-condenser, Jelinek disc and Jelinek "Débourbeur", Greiner's, Schultz's, Kettler's, those of St. Quentin, Schwager, Schiffer, Weiss and Theisen.

The principle of multiple effect evaporation and of multiple re-heating is next developed. As introductory to this problem, explanation is given of the principal multiple systems, such as those of Rillieux, Lexa and Rillieux, Pauly-Greiner, Curin and Weibel-Piccard and emphasizing the economy of the fore-heater. A chapter is devoted to practical considerations, such as the starting, stopping, testing, cleaning and care of the multiple effect; describing normal working, reversing the circulation, frothing, leakages, sugar losses, heavy boiling, economy of juice levels, practical handling of the fore-heater, density regulators and syrup-samplers. The author sounds a warning against the reckless use of acid in the cleaning of the heating surfaces, where the iron is very badly eroded in the misguided zeal to clean well.

Multiples must be cleaned, in the main, by either caustic soda or sodium carbonate. Authentic cases can be cited where the iron walls of multiple units have been reduced from an original thickness of ¾ inch to that of ⅛ inch by excess of acid, constituting a menace to life and meaning the ultimate purchase of a new body. This further accounts for the

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frequent leakages in the red-lead joints, which greatly lowers the efficiency, to 30 per cent. or more. While it is true, as the author states, "the efficiency of the multiple effect becomes almost normal when the calcareous deposits are broken up and reduced in thickness". This is short-lived, as the remaining, uneven scale forms a favorable nucleus for fresh scale to more quickly form; the final use of the scraper repays the time and trouble. After cleaning with acid, the operator is cautioned not to "examine until all the air contained in its interior has been removed, as there would be danger of an explosion". It does not explain why the "air" should explode. The work is somewhat ambiguous when touching upon the chemical side of several questions.

Frequently, mathematical and technical terms are used, which may not be known to the general student, but in all cases are explained later in some other connection; such expressions as "g" and "volume of depression", etc. We note the very practical suggestion of quickly cooling the pan by help of water circulation through coils.

Fully 65 pages are devoted to the calculations relating to the efficiency of the heating surface and the principle of the re-heating by the hot vapors, when the steam is drawn off from the fore-evaporator or from any chamber of the system, as the calorific demand indicates. The infrequent and restricted application of this principle, in part accounts for the very large coal consumption in many American factories. A careful study of this author's work should result in closer economy in the practical working of many existing, defective plants.

In many treatises the apparently formidable mathematics have proved a barrier to the average student. In general they are far from being as difficult as they appear, and, in reality the underlying principles may be best developed by their intelligent use.

The author has purposely avoided the purely mathematical mode of presentation, but has succeeded well in elucidating this difficult subject, perhaps increasing its usefulness by an empirical treatment, aided by concrete examples and simple mathematics. Owing to the large diversity of opinion among authorities, he has considered it most expedient to confine himself to the views set forth by Horsin-Déon, Dessin and Classen. We note the statement under Dessin, "that the evaporation is always the same in each compartment", is not in accord with that of various other experts, who state that it is never the same in each compartment, but progressively increases, while the difference is not great. This point involves a consideration of "self-evaporation", which is a large factor in steam economy and efficiency, in which latter it approaches the ideal.

The advantages of making the heating surfaces the same in all compartments or smallest in the last, are well presented, as is the subject of

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film evaporation or working with only partially filled tubes. By increasing the figures for the fall in temperature and for increase in heating surface efficiency, the author shows mathematically that the efficiency can be increased 90 per cent by lowering the level and affirms that this has been obtained in practice.

The chapters on Graining, Manufacture of Raw Sugar, Curing, Transportation and Storage, Working of After-Products, Crystallization in Motion, Graining of After-Products, Epuration and Return of After-Products to the Juices, to the Pan, and to the Crystallizers, cover about 150 pages, and are exhaustive and conservative discussions of subjects that have attracted a large amount of scientific study and experimentation. The art of sugar-boiling cannot be taught from books, but the writer has succeeded in making the main principles clear. The addition of "soda bisulphid to precipitate sulphid of lime" is evidently intended for sodium bisulphite.

In discussing centrifugals driven by hydraulic motors, it is stated that "these centrifugals have exceptional advantages in case there is ample water power at one's disposal". With the Watson Laidlow machine, the head of water is maintained by a double acting pump, and the water, after discharge from the Pelton driving wheel, returns to the pump supply tank, to be again used. The many factors affecting the successful exhaustion of the original beet-syrup of perhaps 88 to 90 purity until a final molasses of about 60 results, are described in detail. The discussion is interspersed with practical hints and many interesting and important data show the wide field of reading covered. A chapter follows on the manufacture of white sugar, subdivided into granulated, loaf-sugar, cakes and bars, and the sawing and breaking into the various forms.

Under Utilization of Residues is described the recovery of sugar from waste molasses, by Osmosis and by the use of the de-sugarizing chemicals, the hydroxides of calcium, strontium, barium and lead. It is doubtful if these subjects have even been better or more succinctly discussed. While regarding Osmosis favorably the writer does not hesitate to point out its disadvantages.

The process of lime separation is the main feature of the chapter and is thoroughly up to date. Partisans of this process can scarcely take exception to the statement that peculiar effects are said to be produced on the boiling house products by the presence of the saccharate syrup; this is caused largely by mismanagement, as pointed out. In well conducted refineries, so well do the boiling house products work, with saccharate syrup, that for whole seasons nothing but standard white granulated sugar has been produced, from "thick-juice" to final molasses, no raw sugar appearing at any stage. The statement that the Raymond mills,

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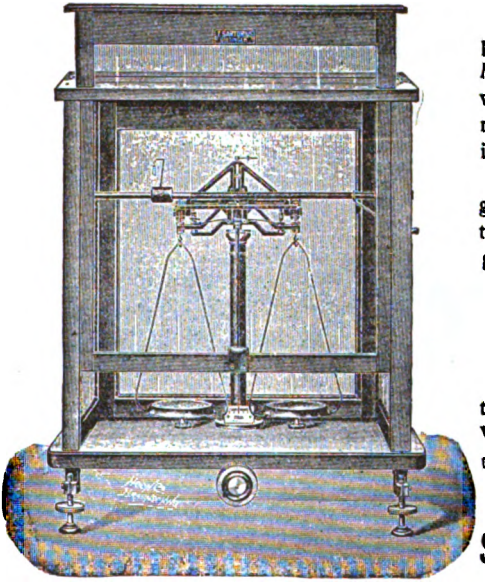
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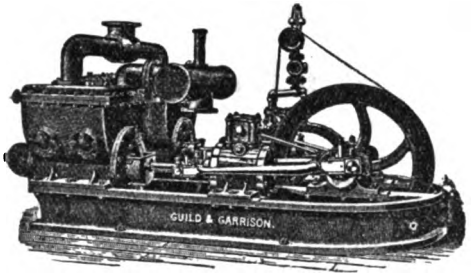
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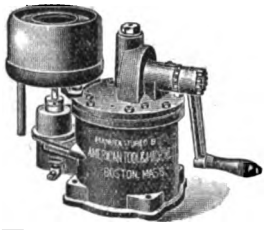
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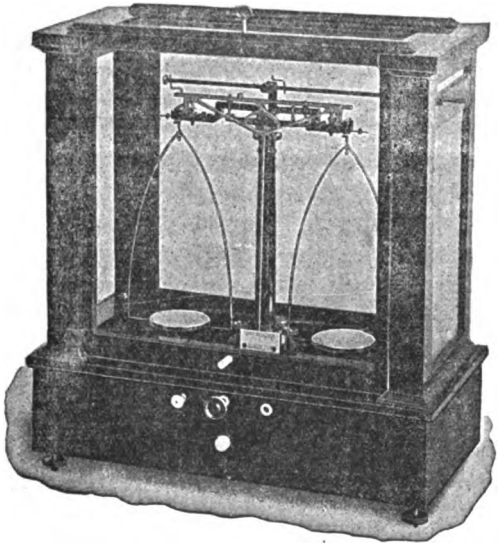
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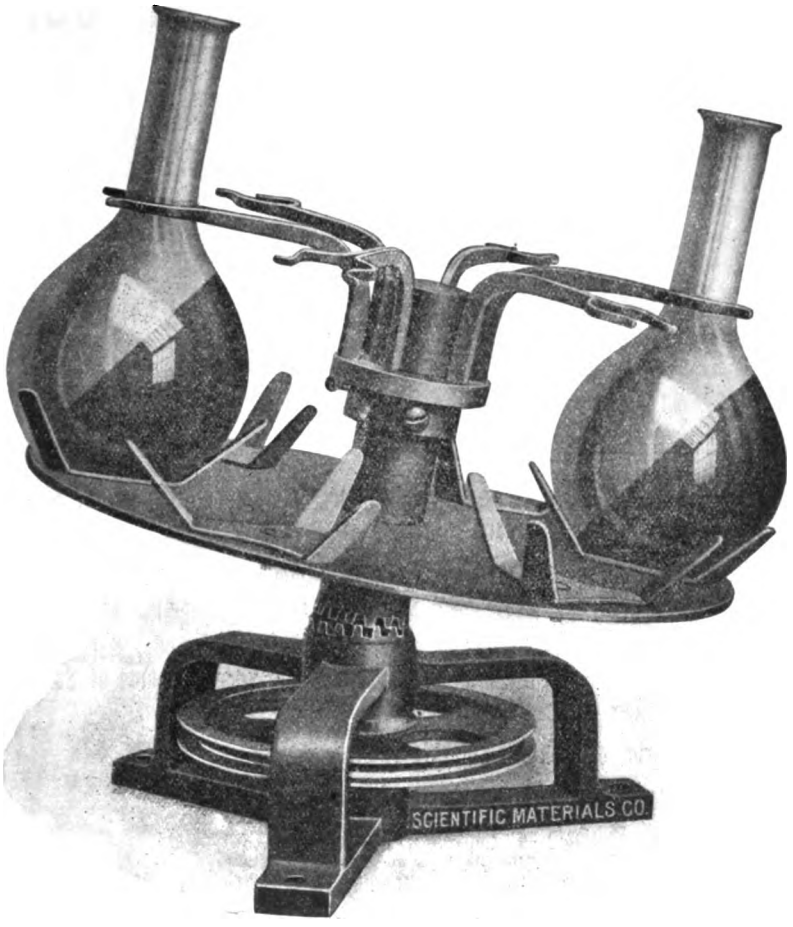
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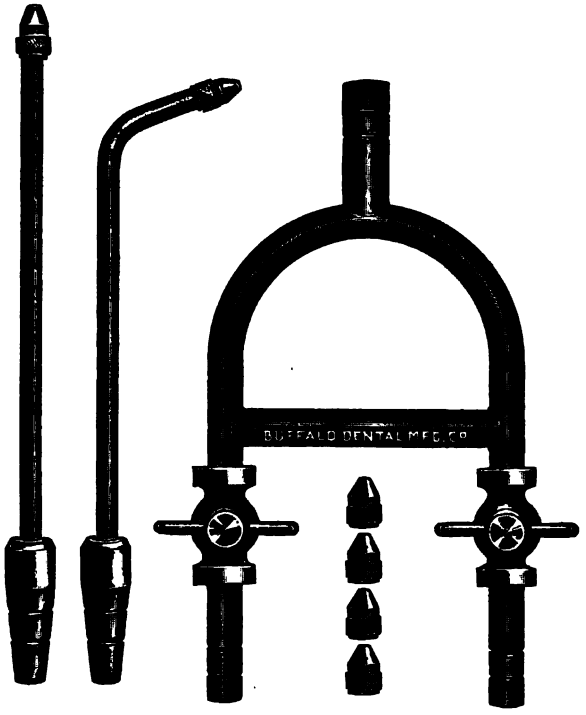
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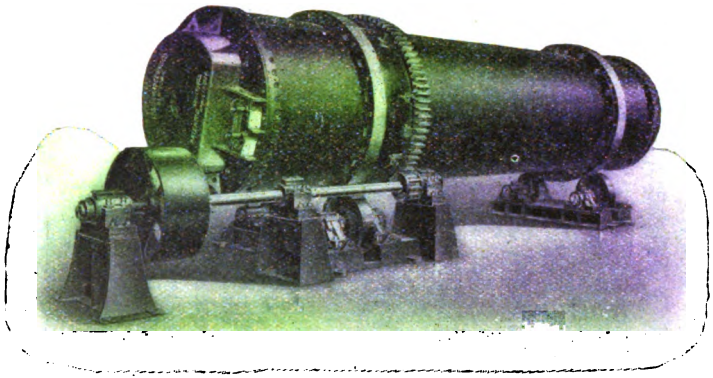
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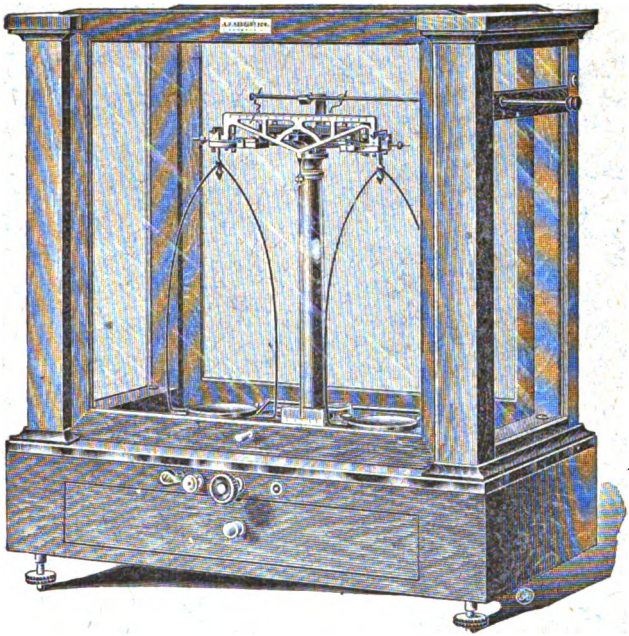
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THE JOURNAL

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THE OCCURRENCE OF HELIUM IN NATURAL GAS AND THE COMPOSITION OF NATURAL GAS.

BY HAMILTON P. CADY AND DAVID F. MCFARLAND.

Received September 10, 1907.

Historical.

During the year 1903, a gas well drilled at Dexter, in Cowley County, Kansas, gave a strong flow of gas, which was found very difficult to burn. A sample was sent to the University of Kansas for analysis, and was found to contain only a small proportion of combustible constituents and a very large proportion of incombustible residue, such as is usually reported in gas analyses as nitrogen. The results of the analysis were published in a paper by Haworth and McFarland,[1] and by McFarland.[2] When the nitrogenous residue, mixed with oxygen, was subjected to the action of an electric spark over a strong solution of potassium hydroxide, for a very long time, there was left a residue which refused to combine with the oxygen, and was evidently not nitrogen. This suggested the presence of some of the inert gases of the Argon group.

Further investigation of the Dexter gas by the methods described in this paper, has shown the presence of considerable quantities of helium, and in a paper read for us by Prof. E. H. S. Bailey, at the New Orleans meeting of the American Chemical Society, we reported 1.84 per cent. helium. Since that time the investigation has been extended to many other Kansas natural gases, and also to gases from other fields, and in nearly every case helium has been found.

Moreover, a method has been worked out by which the percentage of helium may be readily determined, and this has been done in the case of all the gases examined.

[1] Science, 21, 191.

[2] Proc. Kans. Acad. Sci., 19, 60.

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Along with the determination of helium, an extended analysis of each gas has been made to determine its other more common constituents. In all, over forty gases from the Kansas field and from other fields at widely separated parts of the country, have been worked with and complete results are now available from most of these. It is our purpose, in this paper, to present these results with a description of the methods employed in obtaining them and some general facts brought out by their consideration.

Collection of Gases.—Much of the work of collecting the samples of gas for analysis was done by members of the University Geological Survey, and the cost of collection was in most cases borne by the Survey.

Several strong steel and tin cylinders of a variety of shapes and sizes were adapted to the needs of the work. Stop-cocks were put at each end of the cylinder, fitted with caps to prevent leakage. The tin cylinders were shipped in galvanized iron carrying cases, which protected them from injury. At the gas well both ends of the cylinder were opened and one end attached by a secure connection to the source of gas. The gas was then allowed to flow through the cylinder, at a considerable pressure if possible, for several minutes to insure the complete driving out of all air. This was found to be quite effective when properly carried out. Then the stop-cock at the end of the cylinder opposite to that at which the gas was entering was closed tightly and the gas was allowed to accumulate in the cylinder. In the tin cylinders a pressure of fifty pounds was often carried, while in the steel cylinders the entire well pressure of several hundred pounds could be reached. When this maximum pressure had been attained the cylinder was tightly closed and shipped to the laboratory.

When received at the laboratory, enough gas was taken from the cylinder to fill a large glass gasometer in which the gas was confined over distilled water. This constituted the portion for the extraction of helium. At the same time a small flask was filled with gas for the analysis. The determination of helium and the complete analysis were carried out immediately whenever possible, and if any delay was necessitated, it was made as short as possible, and precautions were taken to avoid contamination of the sample or absorption of carbon dioxide.

Methods of Analysis.—For the determination of the constituents of the gas other than the rare elements of the argon group, the standard methods of Hempel were used. In a one hundred cubic centimeter portion of the gas, the determinations were made in the following order. Oxygen was absorbed in a phosphorus pipette; carbon dioxide in strong potassium hydroxide solution, ethylene and the olefines in fuming sulphuric acid, followed by potassium hydroxide, and finally, carbon monoxide in ammoniacal cuprous chloride.

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After the determination of carbon monoxide, a portion of the residue, usually about 20 cc., was measured off, mixed with pure oxygen and air in such a manner as to give a proper excess of oxygen, and exploded over mercury. The contraction in volume, and the amount of carbon dioxide produced were determined in the usual manner, taking precautions to avoid, as much as possible, the error introduced by the absorption of carbon dioxide in the water produced by the explosion, which error may be considerable if haste is not used in the measurement of the volume after explosion. The residual oxygen was then determined by means of the phosphorus pipette in order to show both its amount and also that of the residual nitrogen. Frequent readings of barometer and thermometer, enabled corrections to be made for changes in temperature and pressure.

From the explosion data, the quantities of methane and ethane were calculated, assuming that these were the only paraffin hydrocarbons present; an assumption which is not entirely warranted because of the fact that it was found possible to condense higher boiling hydrocarbons along with the methane in a bulb surrounded by liquid air. Some of these remained liquid up to ordinary temperatures and had an odor similar to that of light boiling petroleum distillates. The quantity of this residue varied in the different gases. It has seemed practically impossible to get at the amounts of these substances by explosion methods, and for the present the above assumption will be made. It seems probable, however, that they may be determined by the fractional distillation of the liquefied gas, and work along this line is being carried on in this laboratory.

For the determination of hydrogen, a portion of the residue from the absorption of carbon monoxide was used. It was found that the data from explosions were entirely too unreliable for the calculation of hydrogen, and the combustion of the hydrogen, mixed with air, over palladinized asbestos, was adopted. In order to insure the combustion of only the hydrogen on heating to a constant temperature of 100°, the U-tube containing palladinized asbestos was surrounded by a Dewar vacuum jacketed tube containing water which was kept at the boiling point by a platinum coil, heated by the passage of an electric current. Several determinations of hydrogen in mixtures of known composition proved the efficiency of this arrangement. With the electrical heating device, a constant temperature could be maintained, while the vacuum jacket around the bath prevented effectually the heating of the apparatus outside the U-tube.

Determination of Helium.—For the determination of helium, use was made of the property of cocoanut charcoal of absorbing all gases except helium, neon and hydrogen, when cooled with liquid air. This prop-

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erty was discovered by Dewar[1]. It is our experience that hydrogen is rather freely absorbed, neon much less than hydrogen, and helium so slightly that all but an infinitesimal trace can be removed by pumping with a mercury pump.

Apparatus.—The apparatus used is shown diagrammatically in Fig. 1. (A) is a condensing bulb, in which, when surrounded by liquid air, the greater part of the methane and other hydrocarbons contained in the natural gas can be liquefied. (B) and (C) are bulbs containing 20 grams of cocoanut charcoal each. (D) and (G) are U-shaped glass tubes which when immersed in liquid air, hold back water and mercury vapors. This is by far the simplest and most effective method of preventing the diffusion of mercury vapor into the spectral tubes used. The actual apparatus is so constructed that D and G may both be immersed in the same vacuum tube. (H) is an automatic Sprengel air pump, the mercury being returned to the reservoir in the form of small drops by the suction of a Chapman pump. (I) is the receiver for collecting helium, (F) and (E) are Plücker tubes. (F) is a permanent part of the apparatus; (E) is filled with the gas and sealed off for later examination with a large spectrometer.

To prepare the apparatus for an analysis, a good water pump was connected to the charcoal bulbs at (J), and dry air drawn through the apparatus to remove all gases left from the previous analysis. The connection with the outer air was then cut off and the whole exhausted as thoroughly as possible with the water pump, heating the charcoal bulbs strongly at the same time. When exhaustion had been carried to the limit of the water pump, the Sprengel pump was put into operation, and the pumping continued until practically all the air had been removed. The charcoal bulbs were allowed to cool and then immersed in liquid air. The vacuum quickly became so good that a spark would not pass through the Plücker tubes. The apparatus was then ready for use.

Method of Analysis.—The gas for analysis was taken from the gasometer containing it and the amount used was determined from the weight of water which displaced it, making all necessary corrections for temperature and pressure. The bulb (A) was first filled with water, inverted, and the water displaced by the gas. It was then surrounded with liquid air and put into connection with the gas holder. If the gas did not contain more than 50 per cent. of nitrogen, from 12 to 15 liters would quickly pass into the bulb. A large amount of nitrogen seems to dissolve in the liquid methane. When the desired amount of gas had passed into (A) the connection with the gas holder was closed and after standing for several minutes the stop-cock leading into (B) was opened for a moment, that between (B) and (C) being closed. The gas was held in B for five

[1] Chem. News, 90, 90 (1904).

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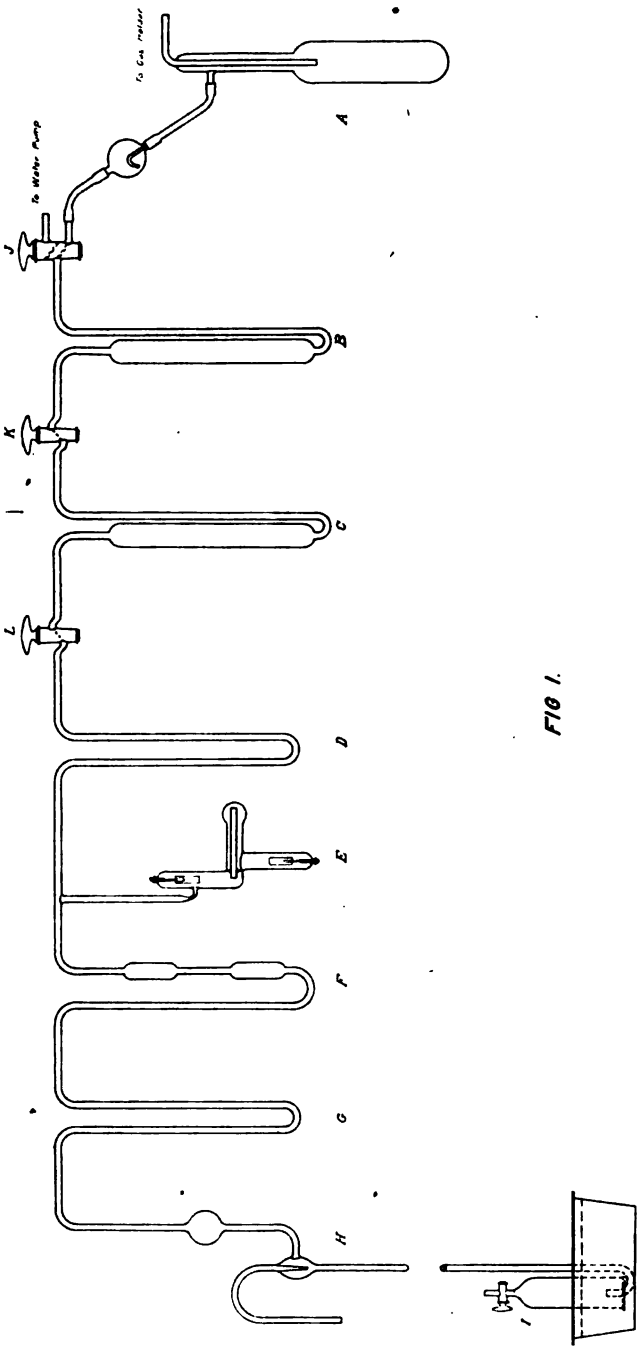


FIG 1.

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minutes to allow the absorption of everything except the helium. Stop-cock L being closed, the gas was passed into C and allowed to stay there another five minutes, and finally admitted to the Plücker tubes and pump. Here it was examined with the spectroscope, removed by means of the pump, and collected in I. When the pressure in the system became low, stop-cock K was closed and more gas admitted into B from A, allowed to stand, passed into C, and finally after standing there the required time, the connection to the pump was again opened. This entire series of operations was repeated until no more helium could be obtained. It has been repeatedly proven by our experience that practically all the helium may be removed by this process. Towards the end of the operation when the pressure in the entire system was low, the liquid methane solution in A could be made to boil even when surrounded by liquid air, and this insured the removal of all the helium from the bulb. It might be mentioned in passing, that the freezing point of the methane was lowered by the nitrogen, etc., so that only part of it solidified in A.

With care all the helium could be transferred to the charcoal bulb without permitting so much nitrogen to pass over as to saturate the charcoal. The purity of the gas could be insured by watching the spectrum and if there was any suspicion of nitrogen the apparatus was prepared as for a new analysis and the gas run through again. The operation was tedious but not more so than most gravimetric determinations.

By essentially the same method, but using larger charcoal bulbs, considerable quantities of helium have been obtained, and a still larger apparatus is being constructed.

That the gas obtained in these experiments is helium, is proven by the fact that all of the visible lines of helium catalogued have been observed, the wave-lengths agreeing within the limits of error, with the accepted values. This is also established by direct comparison of the spectra with those given by known specimens of helium.

The spectrometer in use for the examination of the gases is a new Pulfrich auto-collimating instrument made by Zeiss. It is very powerful and quite satisfactory. Readings can be taken rapidly and the duplicates agree closely.

The new form of end-on tubes made by Goetze, (See E, Fig. 1) when filled with gases of the argon group give beautifully sharp spectra.

The helium obtained as above practically always shows hydrogen lines and carbon bands, the latter, most likely, from a trace of carbon monoxide, but these two impurities are present in such small quantities that the contraction produced on exploding a mixture of the helium with pure oxygen and electrolytic gas, is too small to measure. During the analysis of the gas, no neon was detected, but later, during the preparation of larger quantities of helium from one of the gases, neon was found, as

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will be described in a following paper. The quantity was not determined, but it is certainly small compared to that of helium in the same gas.

Analytical Results.—The results of the analyses are given in the following table (Table 1). The analyses are arranged in the order of the quantity of helium contained in the gases. A statement of such data as were obtainable regarding the location, depth and pressure of the wells producing the gases, as well as other matter of interest regarding their occurrence, is appended to the table.

Data Concerning Collection of Gases Analyzed.

1. Dexter, Kansas. Original sample. Collected in 1905 from well supplying town. Depth 310 feet. Pressure, 110 lbs. Capacity, 6 million feet.

2. Gas from Kansas Natural Gas Co. pipe-line at Lawrence, Kansas. Comes from near Chanute, Kansas. Composite from several wells. Sample taken Oct. 23, 1905, about one week after gas was first turned on.

3. Pipe Line Gas. Same general source as No. 2. Sample taken at Lawrence, May 16, 1906.

4. Eudora, Kansas. Collected from town mains. Comes from wells in town, 350 feet deep. Pressure, 200 lbs.

6. Dexter, Kansas. Greenwell well. Depth and pressure similar to No. 1. Collected June 12, 1906.

7. Iola, Kansas. City supply. Collected from mains at office of Iola Gas Co. June 10, 1906.

8. Moline, Kansas. Collected June 24, 1906. From wells south, east and west of Moline. Average depth, 1150 feet. Av. pressure, 380 lbs.

9. Fredona, Kansas. Town supply. Wells from 2 to 7 miles, east, south and northwest of town. Depth from 1085 to 1250 feet. Pressure from 300 to 480 lbs.

10. Neodesha, Kansas. Collected June 27, 1906. Some air in the sample.

11. Lawrence, Kansas. From an old well, about 1200 feet deep. Only slight flow of gas. Collected July 4, 1906.

12. Erie, Kansas. City supply. From wells north and east of town, within two miles. Depth, 510 feet. Pressure 150 lbs. Sample collected July 3, 1906.

14. Bartlesville, Ind. Ter. Received July 8, 1906. Air in the sample.

15. Bonner Springs, Kansas. Collected July 8, 1906. From wells averaging 600 feet in depth, and 190 lbs. pressure belonging to The Bonner Portland Cement Co.

16. Parsons, Kansas. Gas supplied by pipe-line to city of Parsons. Comes from wells in Eson district in southeastern part of Wilson Co., Kan., belonging to the Prairie Oil and Gas Co.

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TABLE 1.—COMPOSITION OF NATURAL GASES.
Analyses Arranged in Order of Magnitude of Helium Content. Kansas Gases.
(Including Adjacent Missouri and Oklahoma Gases).

No.	Locality	Oxygen O_2	Carbon Dioxide CO_2	Olefines C_2H_4 etc.	Carbon Monoxide CO	Methane CH_4	Ethane C_2H_6	Hydrogen H_2	Helium He	Nitrogen N_2
1	Dexter	0.20	0.00		0.00	14.85	0.41	trace	1.84	82.70
6	Dexter (Greenwell well)	0.10	0.00	0.00	0.00	14.33	1.06	trace	1.64	82.87
41	Eureka new field	0.10	0.20	0.00	0.00	51.80	0.00	0.00	1.50	46.40
42	Eureka town supply	0.50	0.20	0.00	0.00	51.40	0.00	0.00	1.50	46.40
9	Fredonia	trace	0.61	0.12	0.00	82.25	0.00	0.00	0.616	16.40
40	Elmdale	0.30	0.15	0.55	0.00	78.60	7.71	0.00	0.56	12.13
8	Moline	0.00	0.54		0.00	74.10	0.00	trace	0.51	24.85
36	Burlington	0.00	0.00	0.20	0.00	85.50	3.20	0.00	0.495	10.60
27	New Albany	0.00	0.20	0.25	0.00	89.10	0.00	0.12	0.49	9.84
11	Lawrence Deep Well	trace	0.92	0.00	0.00	81.40	0.00	0.00	0.46	17.22
34	Olathe	trace	0.00	0.10	0.00	84.40	0.00	0.00	0.40	15.10
33	Garnett	trace	0.20	0.16	0.00	94.30	0.36	0.00	0.37	4.61
4	Eudora	0.31	0.62	0.00	0.00	88.60	0.00	0.00	0.27	10.20
16	Parsons (Wilson Co.)	trace	0.72	0.00	0.00	91.90	3.37	0.00	0.27	3.74
31	Buffalo	trace	0.00	0.00	0.11	96.20	0.78	0.18	0.27	2.46
28	Altoona	0.00	0.92	0.00	0.00	92.00	2.85	0.00	0.263	3.97
37	Augusta	0.00	0.00	0.77	0.00	79.10	7.44	0.00	0.25	12.44
25	Chanute	0.10	0.00	0.00	0.00	94.70	0.00	0.00	0.24	4.96
20	Moran	0.20	0.30	0.35	0.20	92.00	0.00	0.39	0.214	6.35
23	Peru	0.10	0.51	0.51	0.00	81.70	7.60	0.00	0.19	9.39
7	Iola	0.23	0.00	0.00	0.00	94.50	0.00	trace	0.183	5.08
3	Lawrence Pipe Line Kans. Nat. May 16, '06	trace	0.20		0.00	98.06	0.00	trace	0.17	1.57
2	Pipe Line Oct. 23, '05	0.12	0.00		0.00	98.00	0.00	0.00		1.88
45	Pipe Line Dec. 12, '06	0.24	1.94	0.00	0.00	94.30	0.75	0.00	0.17	2.60
17	Arkansas City	0.20	0.10	0.10	0.00	81.10	11.95	0.00	0.159	6.39
32	Blackwell, Okla.	0.00	0.00	0.61	0.00	83.40	10.31	0.33	0.16	5.19
26	Humbolt	0.10	0.00	0.81	0.00	94.00	1.97	0.00	0.14	2.98
21	Iola	0.40	0.70	0.00	0.30	91.50	0.00	0.00	0.132	6.97
12	Erie	0.22	0.33	0.30	0.00	90.30	4.26	0.00	0.13	4.45
10	Neodesha	No complete analyses							0.106	
15	Bonner Springs	0.10	0.00	0.00	0.00	97.18	0.00	0.25	0.104	2.36
18	Altamont Pipe Line Liberty and Coffeyville	0.00	0.92	0.61	0.00	95.70	0.00	0.00	0.080	2.69
22	Caney	0.15	0.81	0.10	0.00	92.40	0.00	0.00	0.08	6.46
44	Sheffield, Mo.	0.20	0.83	0.50	0.10	92.90	0.00	0.00	0.041	5.43
43	Kansas City, Mo. 2416 Tracy Ave.	0.10	0.60	1.20	0.20	87.20	7.03	0.00	0.013	3.65
35	Paola	0.40	0.70	0.00	0.00	98.00	0.00	0.00	0.0093	0.88
14	Bartlesville, Ind. Ter.	No complete analysis.							He present but not det.	
Gases from Other Fields.										
24	Butler, Ohio	0.05	0.00	0.40	0.00	70.00	16.75	0.27	0.15	12.38
38	Marion, Ind.	0.00	0.73	0.86	0.00	77.40	14.18	0.00	0.167	6.66
39	Morgantown, West Va.	0.00	0.24	0.65	0.00	88.10	7.37	0.25	0.09	3.60
46	Jennings, La. Some air in sample	1.81	1.80	0.80	0.40	88.40	1.03		trace	5.76
47	Los Angeles, Cal. Some air in sample	2.86	6.68	0.20	0.25	83.70	0.00		0.00	6.31

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17. Arkansas City, Kansas. City supply. From well 750 feet deep, with pressure of 355 lbs. and capacity of 5-6 million feet.

18. Altamont. Gas collected from Kansas Natural Gas Company's pipe-line supplying Joplin district. Comes from near Liberty and Coffeyville in Montgomery Co. Coffeyville wells are about 950 feet deep and have a pressure of 450 lbs. Sample is a composite, representing the district.

20. Moran, Kansas. Collected July 13, 1906. No data.

21. Iola, Kansas. City supply. A composite sample from several wells. Collected July 13, 1906, from mains at city gas office.

22. Caney, Kansas. From a well two miles east of Caney. Pressure, 620 lbs. Depth is 1550 feet. Belongs to Caney Gas and Mining Co. Collected July 14, 1906.

24. Butler, Ohio. Richland Co. Collected July 19, 1906, from well belonging to Frank O. Levering. Well pressure is 1200 lbs.

23. Peru, Kansas. Collected July 20, 1906. No data.

25. Chanute, Kansas. City supply. From wells east of city. Composite sample. Depth, 850 feet. Pressure averages 200 lbs. Collected July 24, 1906.

26. Humboldt, Kansas. Composite sample from low pressure mains of city supply. Collected July 23, 1906.

27. New Albany, Kansas. Received July 25, 1906. No data.

28. Altoona. Received July 25, 1906. No data.

31. Buffalo, Kansas. Sample from well inside of town. Collected July 28, 1906.

32. Blackwell, Okla. Received from J. W. Beatty, July 31, 1906. Taken from well No. 2, of Union Gas and Oil Co. Depth 640 feet. Pressure, 185 lbs. Capacity is one million feet.

33. Garnet, Kansas. Sample collected Aug. 1, 1906, from mains bringing in town supply from wells east of town. Av. depth, 600 feet. Av. pressure, 200 lbs.

34. Olathe, Kansas. Sample from city supply. Aug. 2, 1906. Comes from Spring Hill, Kansas (ten miles south of Olathe). Av. depth is 580 feet. Pressure, 184 pounds.

35. Paola, Kansas. City supply. No data. Received Aug. 3, 1906.

36. Burlington, Kansas. Collected Aug. 4, 1906, from high pressure supply pipe bringing in gas for city supply from wells several miles south.

37. Augusta, Kansas. Sample received Aug. 4, 1906. City supply from wells averaging 1440 feet in depth with producing strata at 1200, 1325 and 1420 feet. Av. pressure about 650 lbs.

38. Marion, Indiana. Sample collected by B. A. Kinney, State Supervisor of Natural Gas for Indiana. Received Aug. 25, 1906.

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39. Morgantown, West Virginia. Collected by B. H. Hite, of West Va. Agricult. Exp. Sta., under direction of Dr. I. D. White, State Geologist. From Bowlby well No. 1, 10 miles west of Morgantown. Depth 1800 feet. Pressure, 160 lbs. Collected Aug. 18, 1906.

40. Elmdale, Kansas. Collected Oct. 6, 1906. Wells 150 to 154 feet deep. Pressure, 45 lbs. Capacity nearly one million feet.

41. Eureka, Kansas. City supply. Received Oct. 25, 1906. No data.

42. Eureka, Kansas. City supply. Received Oct. 25, 1906. No data.

43. Kansas City, Mo. No. 2416 Tracy Ave. Well about 300 feet deep. Very low pressure. Yields only gas enough to light one house.

44. Sheffield, Missouri. Composite sample from several shallow wells at the Sheffield Nut and Bolt Works. Initial pressure about 40 lbs. Aggregate production about 1600 cubic feet per day. Used to run gas engine.

45. Pipe Line Gas. Collected from mains of Kansas Natural Gas Co. at Lawrence, Kansas, Dec. 12, 1906. Composite sample coming from various wells, mostly in Allen and Neosho Co.

46. Jennings, Louisiana. Collected by L. Reinecke, Asst. Geologist on La. Geol. Survey, from gas-producing oil well. Received February, 1907. A little air in sample.

47. Los Angeles, Cal. Collected from gas-producing oil well by Chas. R. Fletcher, 534 Stimson Building, Los Angeles. Sample had some air in it.

Discussion of Results.

An inspection of the above table shows that in all cases save one, the Los Angeles gas, helium was found, and it seems very probable that it might have been found in this also if a sufficiently large quantity of gas were taken for analysis. It will be noticed that gas was examined not only from the Kansas field and the adjoining Oklahoma and Missouri fields which are really continuations of the former, but also representative samples from five other gas fields at rather widely separated positions in the country; from West Virginia, Ohio, Indiana, Louisiana, and California.

Since our work has been more particularly with the gases of Kansas we may discuss these at length.

It is at once seen that the composition of these gases varies widely, frequently in places which are but a few miles apart. A case of this kind is found in the gases from Arkansas City and from Dexter, towns only about 20 miles apart, (See Table No. 1). The same phenomenon has been noticed with the oils of Kansas; oil from one side of a town is sometimes of very different composition and properties from that on the other

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side. This is said to be due to the fact that the porous sandstone which carries the oil and gas is not laid down in continuous layers, but in lenticular masses of irregular size and distribution.

In general, the helium content increases with the nitrogen, although a direct proportionality does not appear to exist. Of course the percentage of both decreases as the percentage of total paraffin hydrocarbons increases, although the ratio of helium to nitrogen may increase.

While there is such a wide variation in the composition of the different gases, there is a marked tendency toward regularity in percentage of helium and of total paraffin hydrocarbons, along lines running across the state from northeast to southwest, as may be seen from the two accompanying maps. Figure 2 shows these lines of nearly equal helium con-

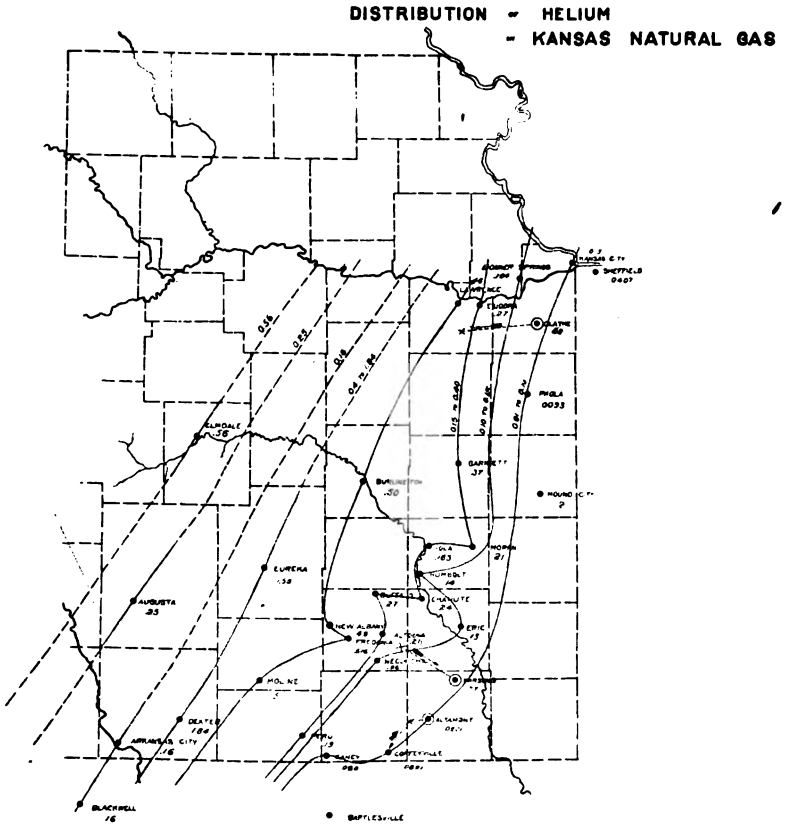


FIGURE 2

tent and Figure 3 shows the lines of nearly equal paraffin content. These lines, which may be called iso-helium and iso-paraffin lines are suggestively similar to the lines showing the outcrop of the various geological

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strata in eastern Kansas. (A map showing the latter may be found in Volume III of the Reports of the University Geological Survey of Kansas; Plates 7 and 8, p. 106.)

The explanation of this regularity of distribution is undoubtedly to be

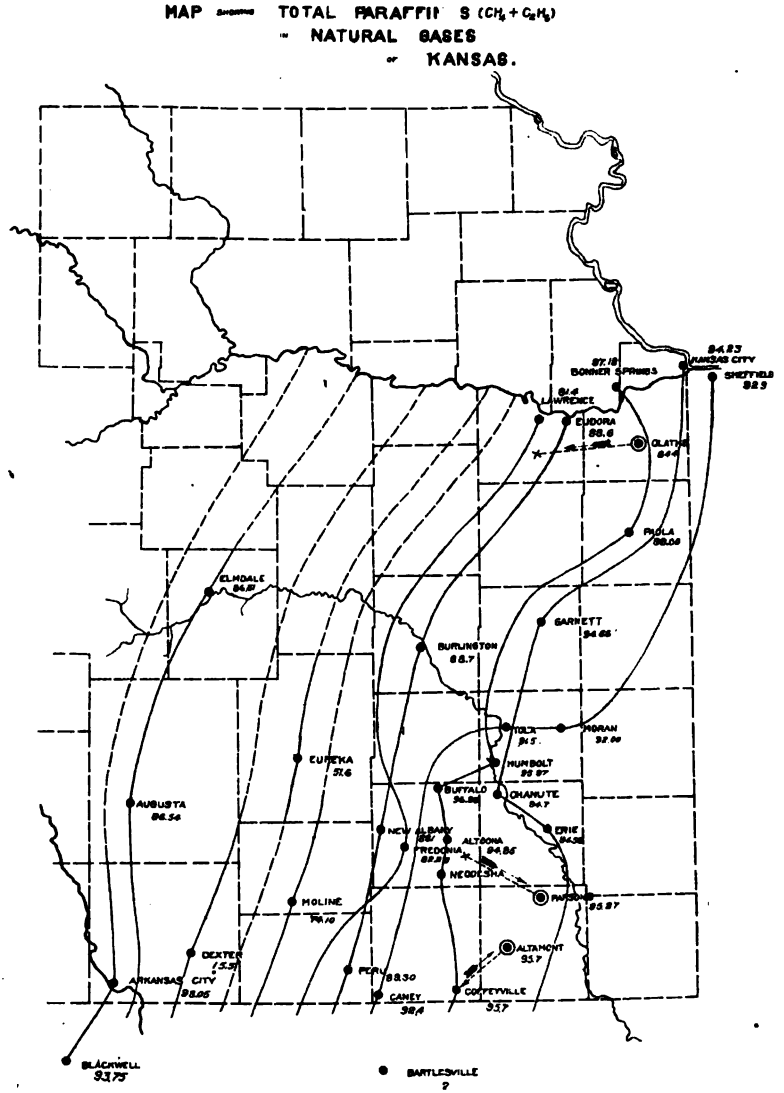


FIGURE 3

found in the arrangement of the strata and the few marked exceptions to this regularity are explainable by the presence of unusual formations at the points where the exceptions occur. This is a matter that is more in the province of the geologist than in that of the chemist.

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The fact that our analyses have shown helium in all but one of the gases examined from various parts of the United States, together with numerous reports of helium having been found in the gases from mineral waters[1] lead us to believe that helium may be found in greater or less quantities in all gases issuing from the earth, and that like many other so-called rare elements, it is really of very wide distribution.

Since Ramsey and Soddy's demonstration of the transformation of radium emanation into helium[2] and Strutt's work[3] showing the very wide distribution of minute percentages of radium in various rocks and soils, it would, of course, occur to everyone that perhaps the helium in natural gases came from the transformation of the emanation derived from the radium. While the percentage of radium is exceedingly small, the aggregate amount is sufficient, granting the transformation, to account for all the helium, provided that sufficient time is given.

If the helium comes from the radium, the percentage of helium in the gas should be proportional to the age of the gas, the radium content of the contributing strata, and inversely proportional to the total quantity of gas. Of course, many other factors would enter into the consideration of this question, such as the rate of diffusion of helium and the accompanying gases, and the fact that the age of the gas cannot always be judged by the age of the strata in which it is found, its position being largely determined by the presence of a sufficiently porous stratum in which it could be stored, and of a difficultly penetrable cap over this stratum.

All of these things make it very difficult to test this hypothesis quantitatively, and at present we wish only to state our belief in its possibility.

Conclusions.

In this paper the results of the examination of 41 samples of natural gas from several widely separated parts of the country are given.

These lead to the following conclusions:

First—That helium is present in all cases except possibly one. It is inferred from this that it is present in all or nearly all of the gases issuing from the earth.

[1] Rayleigh, Chem. News, **72**, 223 (1895); **73**, 247 (1896); Zentralblatt, **1895**, [2] 1112; **1896**, [2] 147. H. Kayser, Chem. News, **72**, 89 (1895); Chem.-Ztg., **19**, 1549 (1905). Bouchard and Troost, Compt. rend., **121**, 392 (1895); Zentralblatt, **1895**, [2] 710. Moureu, Compt. rend., **121**, 819 (1895); **135**, 1335 (1902). F. Pesendorfer, Chem.-Ztg., **29**, 359 (1905). R. Nasini, Atti accad. Lincei (5) **13**, I, 217, 367 (1904); Zentralblatt, **1904**, [1] 1190; [2] 77. Prytz and Thorkelsson, Kgl. Danske Videnski Selsk Forh. **1905**, 317; Zentralblatt, **1905**, [2] 1570. Ewers, Physik. Z., **7**, 224 (1906); Zentralblatt, **1906**, [1] 1319. Moureu and Biquard, Compt. rend., **143**, 795 (1906); Zentralblatt. **1907**, [1] 500. Moureu, Compt. rend., **142**, 1155 (1906); Zentralblatt, **1906**, [2] 156.

[2] Pr. Roy. Soc. London, **72**, 204 (1903); **73**, 346 (1904).

[3] Chem. News, **93**, 235 (1906).

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Second—The helium content of the gas tends to increase as the nitrogen increases, though no direct relation is observed.

Third—In Kansas, lines of iso-helium and iso-paraffin content can be traced across the state and these follow approximately the lines of outcrop of the various geological strata.

Fourth—A very wide variation in composition is noted in the gases examined; hydrocarbons varying from 15.00 per cent. to 98.00 per cent., and helium from a trace up to 1.84 per cent.

LAWRENCE, KANSAS.
August 26, 1907.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 145.]

THE IGNITION TEMPERATURES OF GASEOUS MIXTURES.

SECOND PAPER.

BY K. GEORGE FALK.
Received July 20, 1907.

Introduction.

In a paper published about a year ago[1] a new method was described for determining the ignition temperatures of gaseous mixtures and the results obtained for mixtures of hydrogen and oxygen were given in detail. The ignition temperature was defined as the temperature at which a gaseous mass would ignite if left entirely to itself for some time, the catalytic action of the walls of the vessel in which the gas was enclosed being eliminated. The new method for determining these temperatures consisted of instantaneously compressing the mixtures enclosed in a suitable vessel. This compression raises the temperature of the gas, and, if carried out with sufficient rapidity, is adiabatic, no heat being lost by radiation or conduction. The rise in temperature of the mixture may then be calculated from the initial and final volumes of the gas, its initial temperature, and the ratio of the specific heats of the gas at constant pressure and constant volume. In compressing the mixtures, as soon as the temperature of ignition is reached there is a sudden reaction (explosion), enough force being developed by the reaction to make the determination of the final volume of the mixture a comparatively simple matter as was shown in the first paper.

In the present paper, the results obtained by this method for mixtures made up of carbon monoxide and oxygen; hydrogen, oxygen and nitrogen; carbon monoxide, oxygen and nitrogen; and carbon monoxide, oxygen and hydrogen are given, and the results obtained before for mixtures of hydrogen and oxygen confirmed. In the results given for mixtures of hydrogen and oxygen in the first paper a small correction was overlooked, but this has been introduced here and will be discussed later.

[1] This Journal, 28, 1517.

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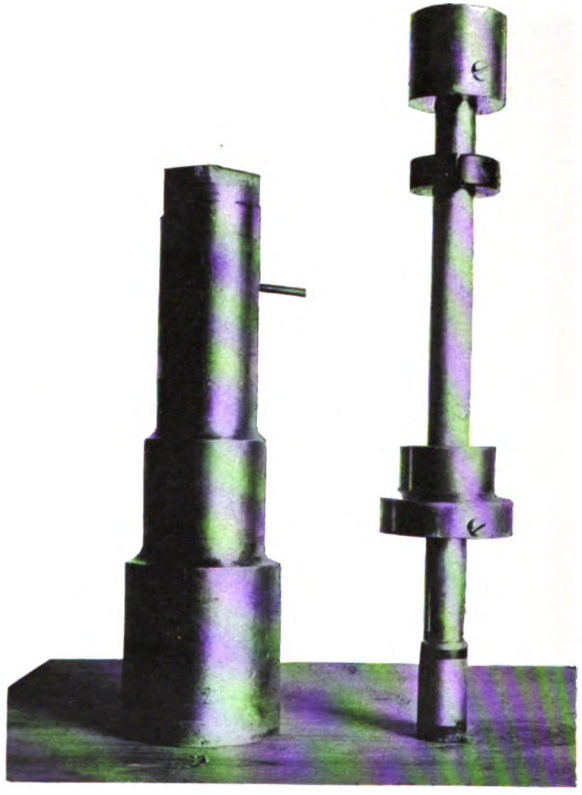


FIG. 1

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Although there has been a considerable amount of work done on the determination of the ignition temperatures of mixtures of hydrogen and oxygen, there has been comparatively little with mixtures of other gases. V. Meyer and Krause[1] found the ignition temperature of the mixture $2CO + O_2$ to lie between 791° and 879° absolute, using the method of enclosing the mixture in sealed bulbs which were plunged into baths heated to definite temperatures. They found the same ignition temperature for the mixture $2H_2 + O_2$. (For a discussion of this method, cf. first paper, p. 1531.) Mallard and Le Chatelier,[2] by passing the gas into a tube heated to a definite temperature, found the ignition temperature of the mixture containing 70 per cent. carbon monoxide and 30 per cent. oxygen to be about 923°. They also found that diluting this mixture, as well as the detonating gas mixture, with one of the active constituents or with an inert gas, modified the ignition temperature only slightly.

Description of Apparatus and Method of Experimenting.

In the determination of the ignition temperatures of mixtures containing hydrogen and oxygen, two pieces of apparatus (I and II) of different sizes were used. In the work to be described here, two new pieces of apparatus (III and IV) entirely of steel, were constructed. Apparatus III is shown in Figure 1.

Apparatus IV is of exactly the same construction, only larger. The general plan of all four is the same, and since I and II were described in detail before, the cut of III and the dimensions of III and IV will suffice here :

	Apparatus III.	Apparatus IV.
Inner length of cylinder	25.460 cm.	24.142 cm.
Inner diameter of cylinder, and diameter of piston head	2.580 cm.	5.078 cm.
Thickness of walls of upper portion of cylinder	1.325 cm.	1.278 cm.
Thickness of walls of lower (thickest) portion of cylinder	2.823 cm.	3.276 cm.
Distance from lower inner edge of inlet tube to bottom of cylinder	19.500 cm.	18.640 cm.
Thickness of steel at bottom of cylinder	3.514 cm.	5.163 cm.
Length of piston	37.688 cm.	36.405 cm.
Volume of gas measured at atmospheric pressure used in each experiment	101.7 cc.	377.5 cc.

With Apparatus I, 69.8 cc. gas were used, with II, 283.9 cc.

The method of experimenting was essentially the same as used before. The mixture was passed into the cylinder through a thin rubber tube passing through the inlet tube, E, the piston being clamped in position so that the lower edge of the piston head was just above the opening of the inlet tube. The air displaced passed out through the inlet tube around the rubber tubing. As soon as sufficient of the mixture had been

[1] Ann., 264, 85.

[2] Annales des Mines (8), 4, 274.

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run in to ensure of the air being completely displaced, the rubber tube was rapidly withdrawn, and the piston pushed down past the opening of the inlet tube. The height of the piston head from the base was then measured, from which the initial volume of the mixture was calculated. To cause adiabatic compression, a weight was dropped on the piston. The device for accomplishing this is shown in Figure 2, which requires no further explanation.

Apparatus IV is shown here ready for an experiment.

By the compression brought about in this way, the piston was forced down until the heat developed by the compression was sufficient to ignite the gas, when an explosion occurred, the entire mass of gas reacting at once, and the downward motion of the piston stopped. From the position of the movable ring, A, which was forced up as the piston descended, the final volume (*i. e.*, the volume at the instant of ignition), was calculated. The ring was made of fiber board and was clamped to the piston rod by a screw by means of which it could be tightened as much as was desired. The piston head was furnished with two leather rings (as shown in Fig. 1), which were renewed when necessary. Lanoline was again used as lubricant, and the two pieces of apparatus were as air-tight as Apparatus II had been found to be. The initial temperature of the mixture was taken to be the room temperature. The initial pressure was always greater than one atmosphere, and was calculated by dividing the distance from the lower edge of the inlet tube to the bottom of the cylinder by h_1, the initial height of the enclosed mixture.

The hydrogen used was obtained in cylinders from Eimer & Amend, and was made from zinc and sulphuric acid. The oxygen was prepared by the S. S. White Dental Manufacturing Company for medicinal purposes, and was the purest obtainable. The carbon monoxide was prepared by dropping formic acid (90 per cent.) into concentrated sulphuric acid, pure carbon monoxide being evolved in large amounts very conveniently by this method. When an inert gas (nitrogen) was used, air was taken and the mixtures calculated on the assumption that it consisted of 80 per cent. nitrogen and 20 per cent. oxygen by volume. Although this is not exactly true, the ignition temperature of a mixture whose composition varies at most 2-3 per cent., as is the case here, is practically constant. This is shown most clearly by the curves for the ignition temperatures of mixtures of hydrogen and oxygen and of carbon monoxide and oxygen. The gases were mixed over water in a two-liter graduated glass gasometer, from which they were run directly into the cylinder, passing through a small wash bottle containing water. In this way the gas was always saturated with water at the ordinary temperature.

Apparatus III was first constructed and used, then Apparatus IV was

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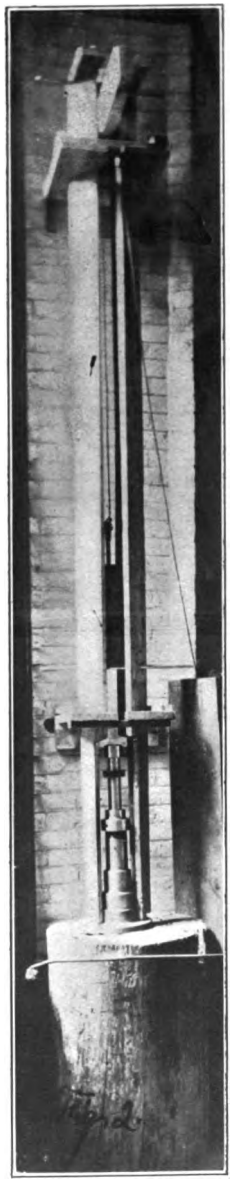


FIG. 2.

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constructed in order to have as greatly differing amounts of gases to work with as possible. It was found, however, that the mechanical difficulties, which need not be detailed here, connected with the use of the larger apparatus, due to the large mass of exploding gas and the consequent violence of the explosion, resulted in so much time being taken up for repairs, etc., that after the results shown in Tables 10 and 16 were obtained, after working two months, this apparatus was abandoned temporarily, since the same results were obtained with Apparatus III, which could be handled much more easily. With Apparatus III, a 22.7 kg. weight was used, with Apparatus IV, a 31.8 kg. weight.

The distances were measured with a steel measuring rod graduated directly to 0.5 millimeters, and carrying a circular vernier with which readings to 0.01 millimeter could be made. The initial height was read to 0.1 millimeter, and the final height to 0.01 millimeter. Although the readings may appear to be more accurate than the method apparently justifies, it was thought best to make the actual experimental measurements as exact as possible.

The experimental work was carried out in the laboratory of Professor Charles E. Lucke, of the Mechanical Engineering Department of Columbia University, and it is due to his aid in assisting to overcome the mechanical difficulties, and in having the repairs which were constantly required made, that it was possible to proceed with this investigation as rapidly as has been the case.

Calculation of Results.

The method of calculating is the same as already given. The formulas used are:

$$\frac{T_2}{T_1} = \left(\frac{h_1}{h_2}\right)^{k-1} \quad \text{and} \quad \frac{p_2}{p_1} = \left(\frac{h_1}{h_2}\right)^{k},$$

in which

T_1 represents the initial (absolute) temperature of the mixture.

T_2, the ignition temperature (absolute).

h_1, the height in centimeters of the initial volume of the mixture (heights may be used in place of volumes since the diameter is constant).

h_2, the final height in centimeters of the mixture (at the ignition temperature).

p_1, the initial pressure of the gas in atmospheres.

p_2, the pressure of the gas in atmospheres at the ignition temperature.

k, the ratio of the specific heats of the gases at constant pressure and constant volume, taken as equal to 1.4 for the gases (H_2, O_2, CO, N_2) used.[1] Since these are diatomic gases, k is the same for all. This brings up the question of a small error which was overlooked in the first

[1] The possible source of error introduced in this way will be discussed later.

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paper. The gases are saturated with water vapor at the ordinary temperature and are then compressed adiabatically. The rise in temperature produced in this way is the same for the diatomic gases, but water vapor being triatomic would not be heated to such a temperature and would consequently lower the temperature of the mixture. Since the gases were saturated at the ordinary temperature (17°-23°) the amount of water vapor present is perfectly definite and may be corrected for. Since $k=1.29$ for water vapor, the rise in temperature of the water vapor as well as of the other gases present may be calculated, and since their specific heats are known by applying the method of mixtures, the temperature of the mixture at the ignition point may be calculated. This ignition temperature would be lower than the one calculated on the assumption that the water vapor had no effect on the heating, but the difference is small. The correction will be applied in detail to one case. The initial temperature being 293° (20° C.) the temperatures produced by the same compression in a diatomic ($k = 1.4$) and in a triatomic ($k = 1.29$) gas are :

$k = 1.4$	$k = 1.29$
736°	571°
842°	630°
931°	678°
1009°	718°

For the mixture $4H_2 + O_2$, Table 1, the average ignition temperature, omitting the correction for water vapor, was calculated to be 874°. The temperature to which water vapor would be raised by the same compression is 647°. One cubic centimeter of the mixture contains 0.072 mg. H_2, 0.286 mg. O_2, and 0.0173 mg. H_2O. The specific heat at constant volume of hydrogen at 874° in thousandths of calories is 2.75, of oxygen at 874°, 0.17, and of water vapor at 647°, 0.38.[1] By the method of mixtures[2], the corrected ignition temperature of the mixture $4H_2 + O_2$ is :

$$\frac{(0.0173 \times 0.38 \times 647) + (0.72 \times 2.75 \times 874) + (0.286 \times 0.17 \times 8.74)}{(0.0173 \times 0.38) + (0.072 \times 2.75) + (0.286 \times 0.17)} = 868°$$

The method is exactly the same for the other mixtures. The corrected final average results will only be given, however. The corrections are small and of the same order of magnitude throughout.

Experimental Results.

Only the corrected results for Tables 1-8 are given. The complete results will be taken up and discussed in groups after the possible sources

[1] Mallard and Le Chatelier, Compt. rend., 96, 1358.

[2] The cooling effect of the water vapor on the gases is of course exerted continuously from the beginning of the compression, but the final result is essentially the same if the total effect is assumed to take place at the final volume, as has been done in the calculations.

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of error have been spoken of. The corrected values of T_2 refer to the correction due to water vapor just explained.

TABLE 1.

$4H_2 + O_2$. Apparatus I.

Corrected T_2 — 868.

TABLE 2.

$2H_2 + O_2$. Apparatus I.

Corrected T_2 — 806.

TABLE 3.

$H_2 + O_2$. Apparatus I.

Corrected T_2 — 781.

TABLE 4.

$4H_2 + O_2$. Apparatus II.

Corrected T_2 — 887.

TABLE 5.

$2H_2 + O_2$. Apparatus II.

Corrected T_2 — 814.

TABLE 6.

$H_2 + O_2$. Apparatus II.

Corrected T_2 — 791.

TABLE 7.

$H_2 + 2O_2$. Apparatus II.

Corrected T_2 — 803.

TABLE 8.

$H_2 + 4\,O_2$. Apparatus II.

Corrected T_2 — 844.

TABLE 9.

$2H_2 + O_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.78	1.076	290.	827.	1.32	51.7
13.48	1.004	291.	822.	1.45	55.0
13.31	0.994	290.	819.	1.47	55.6
13.29	0.979	291.	826.	1.47	56.6

Average 823

Corrected T_2 — 818.

TABLE 10.

$H_2 + O_2$. Apparatus IV.

h_1	h_2	T_1	T_2	p_1	p_2
14.50	1.185	291.	793.	1.29	43.0

Corrected T_2 — 788.

TABLE 11.

$H_2 + O_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.12	0.852	293.	901.	1.38	70.4
13.92	0.906	294.	877.	1.40	64.2
13.75	0.903	294.	874.	1.42	64.2

Average..... 884.

Corrected T_2 — 878.

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TABLE 12.

$6CO + O_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.88	0.669	289.	1000.	1.31	100.8
14.48	0.651	291.	1006.	1.35	103.8
14.31	0.669	291.	991.	1.36	99.1
13.86	0.575	290.	1036.	1.41	121.4
13.33	0.637	290.	979.	1.46	103.1

Average.....1002.

Corrected T_2 — 994.

TABLE 13.

$4CO + O_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
15.70	0.900	290.	910.	1.24	67.9
14.86	0.833	289.	915.	1.31	74.0
14.83	0.837	290.	916.	1.31	73.3
14.09	0.869	292.	890.	1.38	68.1
12.73	0.740	289.	902.	1.52	81.6

Average.....907.

Corrected T_2 — 901.

TABLE 14.

$2 CO + O_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
15.13	0.975	290.	869.	1.29	59.9
14.71	0.891	292.	896.	1.33	67.4
14.63	0.960	290.	862.	1.33	60.3
14.40	0.878	290.	888.	1.36	68.3
13.99	0.908	291.	869.	1.39	67.0
13.80	0.851	293.	893.	1.41	69.8
13.55	0.807	292.	903.	1.44	74.7
13.47	0.887	292.	867.	1.45	65.4
12.37	0.785	291.	877.	1.58	75.0

Average.....880.

Corrected T_2 — 874.

TABLE 15.

$CO + O_2$. Apparatus III.

h_1	h_2.	T_1	T_2	p_1	p_2
15.39	0.860	288.	913.	1.27	72.1
15.35	0.938	292.	893.	1.27	63.6
14.68	0.857	289.	901.	1.33	71.0
14.49	0.861	290.	897.	1.35	70.3
13.87	0.825	290.	897.	1.41	73.3
13.85	0.782	290.	916.	1.41	78.8

Average.....903.

Corrected T_2 — 897.

TABLE 16.

$CO + O_2$. Apparatus IV.

h_1	h_2	T_1	T_2	p_1	p_2
14.88	0.811	289.	925.	1.25	73.4
14.25	0.827	292.	912.	1.31	70.5

Average.....918.

Corrected T_2 — 912.

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TABLE 17.

$H_2 + O_2 + N_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
13.90	1.083	294.	816.	1.40	50.0
13.89	1.046	293.	824.	1.40	52.5
13.78	1.041	294.	826.	1.42	52.6
13.64	1.003	293.	832.	1.43	55.2

Average.....825.

Corrected T_2 — 820.

TABLE 18.

$H_2 + O_2 + 2N_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.60	0.982	292.	860.	1.34	58.5
14.16	0.913	293.	877.	1.38	63.9
14.14	1.007	294.	846.	1.38	55.7
13.80	0.971	293.	847.	1.41	58.1
13.75	0.962	293.	849.	1.42	58.7

Average.....856.

Corrected T_2 — 851.

TABLE 19.

$H_2 + O_2 + 4N_2$. Apparatus III

h_1	h_2	T_1	T_2	p_1	p_2
14.18	0.863	294.	901.	1.38	69.2
14.15	0.808	294.	924.	1.38	75.8
13.92	0.802	294.	921.	1.40	76.1
13.85	0.786	294.	926.	1.41	78.2
13.67	0.815	294.	908.	1.43	73.9

Average.....916.

Corrected T_2 — 910.

TABLE 20.

$2H_2 + O_2 + N_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.65	1.061	294.	840.	1.33	52.5
14.22	1.035	294.	839.	1.37	53.7
14.00	0.957	294.	860.	1.39	59.6
13.84	0.895	292.	873.	1.41	65.2
13.58	0.953	294.	849.	1.44	59.2

Average.....852.

Corrected T_2 — 846.

TABLE 21.

$2H_2 + O_2 + 4N_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.27	0.797	294.	930.	1.37	77.5
14.16	0.829	294.	915.	1.38	73.2
14.10	0.813	294.	921.	1.38	75.1
13.95	0.793	294.	926.	1.40	77.4
13.90	0.736	294.	952.	1.44	87.3

Average.....929

Corrected T_2 — 922.

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TABLE 22.

$H_2 + 2\,O_2 + N_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.10	1.009	294.	844.	1.38	55.5
14.08	0.974	294.	856.	1.38	58.3
14.06	1.051	294.	830.	1.39	52.4
14.04	1.025	294.	838.	1.39	54.8

Average.....842.

Corrected T_2 — 837.

TABLE 23.

$H_2 + 2\,O_2 + 4N_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.26	0.833	293.	913.	1.37	72.9
14.18	0.849	293.	904.	1.38	70.8
13.90	0.753	294.	944.	1.40	83.1
13.85	0.824	294.	909.	1.41	73.2
13.20	0.734	293.	931.	1.48	84.4

Average.....920.

Corrected T_2 — 914.

TABLE 24.

$2CO + O_2 + N_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.03	0.806	293.	919.	1.39	75.9
13.90	0.819	293.	910.	1.40	73.9
13.78	0.786	293.	921.	1.42	78.0
13.28	0.719	293.	941.	1.47	87.1

Average.....923.

Corrected T_2 — 917.

TABLE 25.

$2\,CO + O_2 + 2N_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.05	0.708	293.	968.	1.39	91.0
13.72	0.691	293.	968.	1.42	93.3
13.22	0.712	293.	943.	1.48	88.1
12.95	0.631	293.	981.	1.51	103.4

Average.....965.

Corrected T_2 — 958.

TABLE 26.

$CO + O_2 + N_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.12	0.691	293.	980.	1.38	94.3
13.96	0.689	293.	976.	1.40	94.3
13.63	0.621	293.	1008.	1.43	108.0
13.37	0.656	293.	979.	1.46	99.3

Average.....986.

Corrected T_2 — 979.

TABLE 27.

$CO + O_2 + 2N_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.96	0.544	293.	1103.	1.30	134.9
14.38	0.496	291.	1119.	1.36	151.2
13.98	0.581	292.	1042.	1.39	119.8
12.48	0.441	292.	1112.	1.56	168.4

Average.....1094.

Corrected T_2 — 1085.

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TABLE 28.

$4CO + O_2 + N_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.53	0.773	292.	944.	1.34	81.6
13.96	0.771	292.	930.	1.40	80.6
13.94	0.789	292.	921.	1.40	78.0
13.34	0.735	292.	931.	1.46	84.6

Average.....932.

Corrected T_2 — 925.

TABLE 29.

$4\,CO + O_2 + 2N_2$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
15.22	0.819	292.	940.	1.28	76.6
14.58	0.787	292.	939.	1.34	79.6
13.90	0.733	292.	947.	1.40	86.1
13.63	0.692	292.	962.	1.43	92.8

Average.....947.

Corrected T_2 — 940.

TABLE 30.

$H_2 + O_2 + CO$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.30	1.081	294.	826.	1.36	50.7
14.13	1.075	294.	824.	1.38	50.8
14.02	1.104	294.	813.	1.39	48.8
13.98	1.093	294.	815.	1.39	49.5
13.76	1.075	294.	815.	1.42	50.3
13.74	1.101	294.	807.	1.42	48.6

Average.....817

Corrected T_2 — 812

TABLE 31.

$H_2 + O_2 + 2CO$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.19	0.974	294.	858.	1.37	58.5
14.16	1.019	294.	842.	1.38	54.8
14.03	0.965	294.	858.	1.39	58.9
13.94	0.923	294.	871.	1.40	62.6
13.63	0.955	294.	851.	1.43	59.1

Average.....856.

Corrected T_2 — 851.

TABLE 32.

$H_2 + O_2 + 4\,CO$. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.24	0.891	294.	891.	1.37	66.3
13.93	0.831	294.	908.	1.40	72.5
13.90	0.822	294.	911.	1.40	73.5
13.84	0.815	294.	913.	1.41	74.3
13.78	0.852	294.	895.	1.42	69.7

Average.....904.

Corrected T_2 — 898.

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TABLE 33.

$2H_2 + O_2 + 2$ CO. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.63	0.883	294.	904.	1.33	67.9
14.18	0.921	293.	875.	1.38	63.2
13.91	0.862	293.	891.	1.40	68.8.
13.86	0.901	293.	874.	1.41	64.6
13.54	0.893	294.	872.	1.44	64.8

Average.....883.

Corrected $T_2 - 877$.

TABLE 34.

$2H_2 + O_2 + 4$ CO. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.19	0.749	294.	954.	1.37	84.5
14.09	0.756	293.	944.	1.38	83.1
13.78	0.771	294.	932.	1.42	80.1
13.76	0.716	294.	959.	1.42	88.8
13.66	0.750	293.	936.	1.43	83.0

Average.....945.

Corrected $T_2 - 938$.

TABLE 35.

$H_2 + 2O_2 + 2$ CO. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.02	0.942	293.	863.	1.39	61.0
13.98	0.857	293.	895.	1.39	69.6
13.87	0.947	293.	857.	1.41	60.2
13.86	0.919	293.	867.	1.41	62.8
13.85	0.855	293.	893.	1.41	69.5

Average.....875.

Corrected $T_2 - 869$.

TABLE 36.

$H_2 + 2 O_2 + 4$ CO. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.42	0.845	292.	908.	1.35	71.8
13.98	0.895	292.	877.	1.39	65.4
13.91	0.844	292.	896.	1.40	70.9

Average.....894.

Corrected $T_2 - 888$.

TABLE 37.

$2 H_2 + 3 O_2 + 2$ CO. Apparatus III.

h_1	h_2	T_1	T_2	p_1	p_2
14.59	1.051	291.	834.	1.34	53.1
13.75	1.039	291.	818.	1.42	52.7
13.17	0.947	290.	831.	1.48	59.0
12.61	0.887	289.	836.	1.55	63.6

Average 830.

Corrected $T_2 - 825$.

The initial temperatures of the mixtures can have no effect on their ignition temperatures. This was shown in the first paper and the proof will therefore not be repeated. The effect of the pressure of the gas in any mixture on the ignition temperature of this mixture is so slight, if it exists

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at all, that it could not be determined from the experiments. (This, of course, refers directly only to the high pressures at which the ignition temperatures were determined, but theoretically, as shown in the first paper, the pressure should cause only small differences in these temperatures).

Possible Sources of Error.

In discussing the possible sources of error, the method of calculating is the first to suggest itself, as to whether it is justifiable to assume k equal to 1.4 between the ordinary temperature and the temperature of ignition. Although the earlier work on this subject showed a considerable decrease in k with rising temperature, more recent work especially by Kalähne[1] indicated a different result. Kalähne found, working with air by the "resonance method" that at 723° (450° C.) no decrease in k could be observed, and that at 1173° (900°C.) k=1.39, the decrease being so small that only the most accurate measurements would show it. There has been no recent work on hydrogen and carbon monoxide at high temperatures, but the results obtained for air can doubtless be applied to them as well. It appears then that k varies from a value slightly greater than 1.40 to a value of about 1.395 for the temperatures used here. Increase in pressure, however, increases the value of k slightly, so that 1.4 differs from the true value of k as used in this work by not more than 0.1 per cent. The correction introduced by the water vapor has already been spoken of and applied to the results. The ignition temperatures are all affected equally by it.

In the compressions used in this work, there is a possibility of waves of compression and reflection being set up in the cylinder during the downward motion of the piston.[2] These waves would cause the temperature of the mixture to be higher than that calculated by the ordinary adiabatic formula. There is no expression which takes into account these waves, which may be considerable, and if so, would invalidate the results. The experimental results show, however, that this is not the case. The initial height, h_1 varied for the different mixtures and even for the same mixture. The effect caused by the waves would differ greatly for the different heights, if this effect was in any way large. The experimental work, however, shows that no regular differences can be perceived with different values of h_1, so that this effect must be very small. Whatever error is introduced in this way, would make the calculated temperatures slightly too low.

In dropping the weight on the piston, there is a possibility of the explosion not developing sufficient force to stop the downward motion of

[1] Ann. Phys., 11, 225 (1903).

[2] The possibility of this and the following error were also pointed out to the writer by Professor E. Jouguet.

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the piston immediately. This has already been spoken of (cf. first paper), and it was shown (in detail in Table 2), that dropping the weight from different heights made no practical difference in the ignition temperatures. There remains the possibility of a small constant error, however. This would tend to make the calculated temperatures slightly higher than the actual ignition temperatures, that is, the error would lie in the opposite direction from the former and would tend to neutralize it. These two sources of error, if they exist at all, must be small and act in opposite directions, so that the effect on the ignition temperatures as calculated is entirely negligible.

That there is no radiation or loss of heat in any other way during compression is true because the four pieces of apparatus differing so much in size give essentially the same results.

Discussion of Results.

In the following discussion of results, when the ignition temperature of a mixture was determined in more than one apparatus, the average result obtained with the different sizes was taken. It is impossible to state with certainty that one piece of apparatus gave more accurate results than another, and in any case the results differ by such small quantities that any other way of averaging would show no appreciable difference. The numbers in parentheses refer to the tables which give the details of the experiments.

TABLE A.

HYDROGEN AND OXYGEN.

	T_2
$4H_2 + O_2$ (1, 4, 11)	878
$2H_2 + O_2$ (2, 5, 9)	813
$H_2 + O_2$ (3, 6, 10)	787
$H_2 + 2O_2$ (7)	803
$H_2 + 4O_2$ (8)	844

The following curve (I) shows the ignition temperatures of the different mixtures of hydrogen and oxygen.

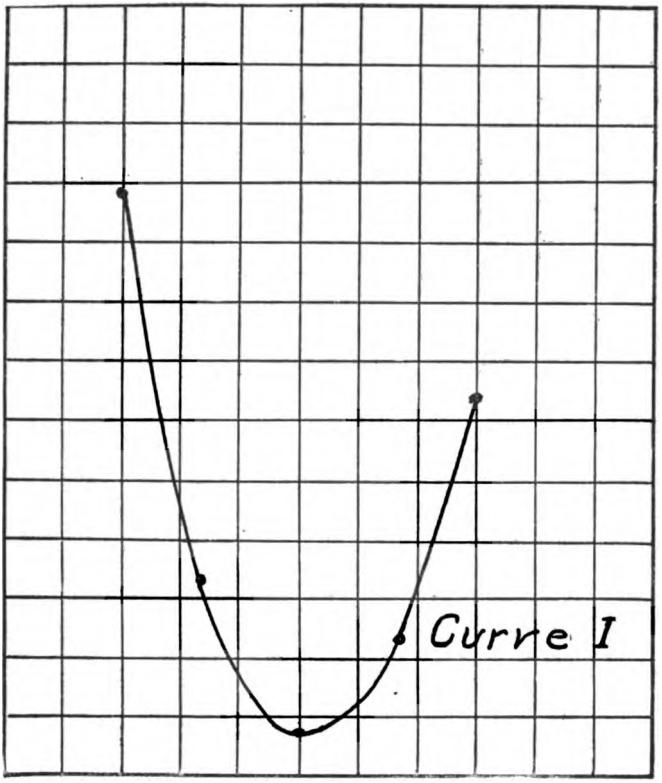
The fact that the maximum affinity is shown by the mixture $H_2 + O_2$ proves that H_2O_2 must be the first product of the reaction between hydrogen and oxygen. This was spoken of in detail in the first paper.

TABLE B.

CARBON MONOXIDE AND OXYGEN.

	T_2
$6\,CO + O_2$ (12)	994
$4\,CO + O_2$ (13)	901
$2\,CO + O_2$ (14)	874
$CO + O_2$ (15, 16)	904

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From the curve (II) and by extrapolation as shown in the dotted portion, the ignition temperatures of different mixtures of carbon monoxide and oxygen can be determined.

The maximum affinity is shown by the mixture $2CO + O_2$, doubling the carbon monoxide or the oxygen, causing the same rise in the ignition temperatures of the resulting mixtures.

TABLE C.

HYDROGEN, OXYGEN AND NITROGEN.

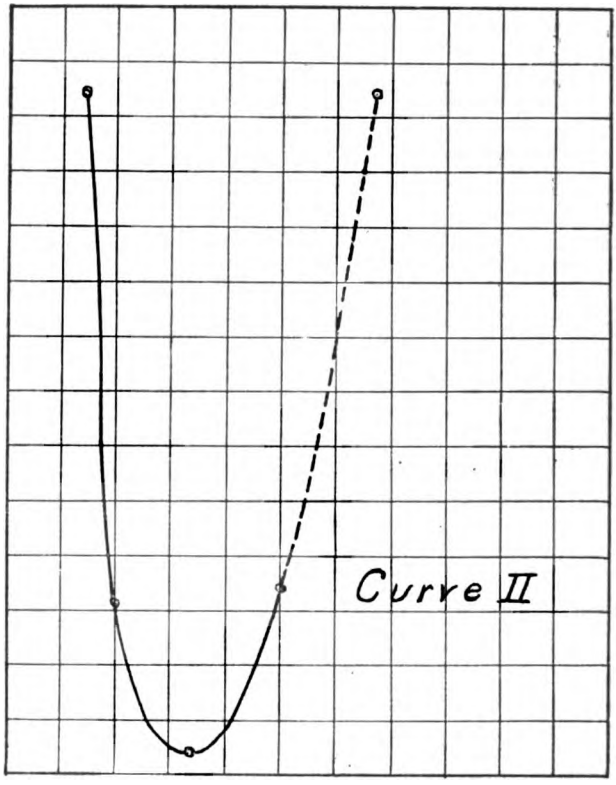
	T_2 (obs.)	T (calc.)
$H_2 + O_2 + N_2$ (17)	820	817
$H_2 + O_2 + 2N_2$ (18)	851	847
$H_2 + O_2 + 4N_2$ (19)	910	907
$2H_2 + O_2 + N_2$ (20)	846	843
$2H_2 + O_2 + 4N_2$ (21)	922	933
$H_2 + 2O_2 + N_2$ (22)	837	833
$H_2 + 2O_2 + 4N_2$ (23).....	914	923

The values of T (calc.) are obtained by means of the empirical equation :

$$(a) \quad T = T_c + 30n,$$

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T denoting the calculated ignition temperatures, T_c the ignition temperatures of the pure hydrogen-oxygen mixtures as obtained from Curve 1,



and n, the volume of the inert gas divided by the lesser volume, of the two active constituents.

$$\left(n = \frac{\text{volume inert gas}}{\text{volume of } H_2 \text{ or } O_2 \text{ (whichever is present in smaller amount)}}\right)$$

Since nitrogen acts only as an inert gas, the above equation (a) taken in conjunction with curve 1, allows the ignition temperature of any mixture of hydrogen and oxygen, alone or in the presence of an inert gas to be calculated very simply. This equation does not say anything about the limit of inflammability, but such a limit must exist for the mixtures containing a large excess of one of the constituents.

TABLE D.

CARBON MONOXIDE, OXYGEN AND NITROGEN.

	T_2 (obs.)	T (calc.)
$2CO + O_2 + N_2$ (24).....	917	914
$2CO + O_2 + 2N_2$ (25).....	958	954
$CO + O_2 + N_2$ (26).....	979	984
$CO + O_2 + 2N_2$ (27).....	1085	1064
$4CO + O_2 + N_2$ (28).....	925	921
$4CO + O_2 + 2N_2$ (29).....	940	941

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The values T (calc.) are obtained by means of the empirical equation

$$(b) \quad T = T_c + 80n'$$

in which T denotes the calculated ignition temperatures, T_c, the ignition temperatures of the mixtures without the inert gas as obtained from curve II, and $n' = \frac{\text{volume inert gas.}}{\text{volume carbon monoxide.}}$ With the aid of curve II and equation (b), the ignition temperature of any mixture of carbon monoxide and oxygen, alone and in the presence of an inert gas, may be calculated up to the point where ignition is impossible.

TABLE E.

HYDROGEN, CARBON MONOXIDE AND OXYGEN.

	T (obs.)	T_a (calc.)	T_b (calc.)
$H_2 + O_2 + CO$ (30)	812	817	984
$H_2 + O_2 + 2CO$ (31)	851	847	914
$H_2 + O_2 + 4CO$ (32)	898	907	921
$2H_2 + O_2 + 2CO$ (33)	877	873	954
$2H_2 + O_2 + 4CO$ (34)	938	933	941
$H_2 + 2O_2 + 2CO$ (35)	869	863	944
$H_2 + 2O_2 + 4CO$ (36)	888	923	894
$2H_2 + 3O_2 + 2CO$ (37)	825	822	1030

The values under T_a (calc.) were obtained from equation (a) and curve I, assuming carbon monoxide to act as a neutral gas, under T_b (calc.) from equation (b) and curve II, assuming hydrogen to be neutral. As seen from the table, the experimentally determined value agrees in every case with the lower of the calculated values, indicating that the ignition temperature is fixed by two of the constituents, the third simply acting as an inert gas. This evidently holds also if nitrogen, carbon dioxide, or any other inert gas is present, so that to calculate the ignition temperature of any mixture of hydrogen, carbon monoxide, oxygen, and an inert gas, it is simply necessary to calculate first the ignition temperature of the hydrogen and oxygen, assuming the rest of the mixture to be inert (curve I, equation (a)), and then, to do the same with the carbon monoxide and oxygen with the other constituents inert (curve II, equation (b)). The lower of these two temperatures will be the required ignition temperature of the mixture.

A number of experiments were tried with hydrogen and nitrogen, nitrogen and oxygen, and carbon monoxide and hydrogen mixtures, but in no case could any sign of a reaction having taken place under the conditions described, be perceived.

Producer gas which is used in gas engines consists essentially of hydrogen, carbon monoxide, oxygen, nitrogen, and carbon dioxide. The results given in this paper show how the ignition temperature of any such mixture may be calculated. A general discussion of this phase of the subject would not be of much value without a large number of

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analyses of the gas and a complete account of the working of the engine.

Some light may also be thrown on the causes of explosions in mines by the results given here.

Theoretical.

Consider a bimolecular reaction taking place in a homogeneous gaseous system. Let r denote a definite volume of the mixture at the ignition temperature, x the part by volume of one of the constituents, y that of the other ($x + y = r$). Then, if v denotes the velocity of the reaction at the ignition temperature, and k the correspon ding velocity constant,

$$v = kxy = kx\,(r - x)\ .$$

$$\frac{dv}{dx} = -kx + k(r - x) = 0\ .\ .\ x = \frac{r}{2} \text{ and } y = \frac{r}{2};$$

or, for the velocity at the ignition temperature to be a maximum, the two constituents must be present in equal volumes or parts by volume. The maximum velocity of reaction evidently corresponds to the greatest affinity, or to the lowest ignition temperature of a mixture containing these two constituents. Conversely, if a mixture of two gases shows the lowest ignition temperature when these gases are present in equal volumes, the reaction between them must be bimolecular. The lowest ignition temperature for mixtures containing oxygen and hydrogen was found for the mixture containing equal volumes of the two gases. The reaction between them is therefore one of the second order. Bodenstein[1] measured directly the velocity of the reaction between hydrogen and oxygen and concluded it to be trimolecular, but Rowe[2] on recalculating Bodenstein's results, found the constant to agree just as well for a bimolecular as for a trimolecular reaction. He assumes, however, that since hydrogen peroxide is decomposed with very great rapidity at higher temperatures[3] it is incapable of being formed at all at these temperatures, and that the reaction is therefore trimolecular The results obtained by determining the ignition temperatures of the different mixtures of hydrogen and oxygen, show that the reaction must be bimolecular and that hydrogen peroxide is the first product formed, although it may decompose again immediately.

The ignition temperature corresponds to a certain definite reaction velocity. If an inert gas is present, the velocity of the reaction between the two gases will be less at the former ignition temperature, and a higher temperature will be required to reach the required velocity and cause ignition.

With the bimolecular reaction just considered, $v = kx(r - x)$ or with

[1] Z. physik. Chem., 29, 665.

[2] Z. physik. Chem., 59, 41. In the review of this paper in Chemical Abstracts 1907, 1662, owing to a printer's error, "bimolecular" appears in place of "trimolecular."

[3] Nernst, Z. physik. Chem., 46, 720.

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equal volumes of the gases present, $x = \frac{r}{2}$, and $v = \frac{kr^2}{4}$. Assume an inert gas, occupying one-third of the volume r to be present. Then $x_1 + y_1 = \frac{2r}{3}$, and for the maximum velocity v_1, $x_1 = y_1 = \frac{r}{3}$. Then $v_1 = k_1 x_1 y_1 = k_1 x_1 \left(\frac{2r}{3} - x_1\right)$. At the ignition temperature of the mixture containing no inert gas, $k_1 = k$, and $v_1 = \frac{kr^2}{9}$, or the velocity of the reaction with the inert gas present will be $\frac{4}{9}$ thus $\left(\text{since } \frac{v_1}{v} = \frac{\frac{kr^2}{9}}{\frac{kr^2}{4}} = \frac{4}{9} \right)$ of the reaction velocity of the pure mixture at the ignition temperature of the latter. To increase the velocity of the former until the velocity of the latter (or ignition) is attained will require a rise in temperature. Experimentally this was found to be 30° (equation (a)). A rise in temperature of 10° for this mixture increases the velocity of the reaction by, $\sqrt[3]{\frac{9}{4}}$, or the velocity coefficient is equal to 1.31 between the limits 787° and 820° (the ignition temperatures of the mixtures $H_2 + O_2$ and $H_2 + O_2 + N_2$).

The effect of the pressure on the ignition temperature, which must also be considered, should be small according to the theoretical view developed by Nernst.[1] This is born out by the experiments on any one mixture, but it must be remembered that the final pressures, p_2 given in the tables represent only an upper limit, since whatever leakage took place between the time of enclosing the gas in the cylinder and of igniting it, tended to decrease the value of p_1, the initial pressure, and therefore also of p_2. The effect of these pressures on comparing the reaction velocities of different mixtures has been entirely disregarded in the theoretical treatment, but this effect would decrease the velocity coefficient for a 10° rise only slightly, as the pressures at which the ignition temperatures were determined were high and with the exception of a few mixtures, of approximately the same magnitude.

Returning to the temperature coefficient of the reaction velocity, the following table shows some of the values calculated, together with the ignition temperatures of the mixtures which show within what temperature limits these values hold :

	Temperature coefficient per 10° rise	Between the temperature limits
($H_2 + O_2$ and $H_2 + O_2 + N_2$)	1.31	787. — 820.
($H_2 + O_2 + N_2$ and $H_2 + O_2 + 2N_2$)	1.21	820. — 851.
($H_2 + O_2 + 2N_2$ and $H_2 + O_2 + 3N_2$)	1.16	851. — 880. (approx.)
($H_2 + O_2 + 3N_2$ and $H_2 + O_2 + 4N_2$)	1.13	880. — 910.

[1] This Journal, 28, 1519.

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The temperature coefficient decreases from 1.31 at about 800° to 1.13 at about 900°. A list of the ratios of the velocities for a number of reactions at intervals of 10° is given by van't Hoff.[1] These ratios do not differ much for different reactions, and are almost all between 2. and 3. for temperatures not far removed from the ordinary temperature. For two reactions, however, the ratios are given for higher temperatures; for the decomposition of phosphine between the temperatures 583° and 785°, the ratio per 10° rise is 1.2, and for the decomposition of arsine, the ratio between 529° and 640° per 10° rise is 1.23. These temperature coefficients (or ratios) are very nearly the same as those found for the reaction between hydrogen and oxygen.

The effect of adding an excess of one of the active constituents will now be considered. If one of these (x) is present in double the quantity of the other (y), then $x + y = r$, but $x = \frac{2r}{3}$ and $y = \frac{r}{3}$ and $v_2 = k_2xy = \frac{2k_2r^2}{9}$ (since the reaction is bimolecular). Applied to the hydrogen-oxygen mixtures for equal volumes of hydrogen and oxygen $v = \frac{kr^2}{4}$, and therefore at the same temperature ($k = k_2$), $\frac{v_2}{v} = \frac{8}{9}$. For the mixtures $H_2 + O_2$ and $H_2 + O_2 + N_2$ as shown before $\frac{v_1}{v} = \frac{\frac{kr^2}{9}}{\frac{kr^2}{4}} = \frac{4}{9}$, a rise of 30° being sufficient to increase the velocity of v_1 so that it becomes equal to v. The ratio of $\frac{v_2}{v}$ is half as great as the ratio $\frac{v_1}{v}$ so that half the rise in temperature, or 15°, should equalize the velocities. With the mixture $4H_2 + O_2$ or $H_2 + 4O_2$, similarly $v_3 = k_3 \cdot \frac{4r}{5} \cdot \frac{r}{5} = \frac{4k_3r^2}{25}$, and when $k_3 = k$, $\frac{v_3}{v} = \frac{16}{25}$. Since 15° corresponds to an increase in velocity of $\frac{1}{9}$, to correspond to an increase of $\frac{9}{25}$, $15 \times \frac{\frac{9}{25}}{\frac{1}{9}} = 49°$ should be required. The calculated and experimentally determined temperatures are as follows:

[1] Chemical Dynamics, Translation by Lehfeldt, p. 228.

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Experimental		Calculated
$H_2 + O_2$	787.	
$H_2 + 2O_2$	803.	802.
$2H_2 + O_2$	813.	
$H_2 + 4O_2$	844.	836.
$4H_2 + O_2$	878.	

The ignition temperatures of the mixtures containing an excess of oxygen agree fairly well with the calculated ignition temperatures, those containing an excess of hydrogen do not agree at all. In fact the mixtures containing an excess of hydrogen agree better if the hydrogen in excess of that required to react with the oxygen is assumed to be inert, the mixture $H_2 + O_2 + 3H_2$ corresponding to the mixture $H_2 + O_2 + 3N_2$, etc. There is at present no explanation for this abnormality (from the theoretical point of view) on the part of the hydrogen.[1] The only certain feature appears to be the fact that an excess of hydrogen or oxygen should affect the ignition temperature of the mixture $H_2 + O_2$ equally which is not the case, and to judge from theoretical considerations and from the experimental work, the cause of the abnormality is the hydrogen. It must be borne in mind, however, that the methods of calculating the ignition temperatures of different mixtures (Curve I, Equation (a)) based upon purely experimental work, hold true, even if the theoretical views at present are not sufficiently developed to support the conclusions arrived at from the experiments.

The same method of treatment may be applied to a trimolecular reaction. Since the experimental data are at hand for the reaction between carbon monoxide and oxygen, a reaction in which two molecules of one constituent react with one of another will only be considered, although, of course, the reasoning may be applied to other cases as well. Let x represent the amount of the former substance present and y of the latter, both measured as fractions of a definite volume r, then the velocity of the reaction at the ignition temperature will be (k being constant for this temperature):—

$$v = kx^2y = kx^2(r - x),$$

$$\frac{dv}{dx} = 2kx(r - x) - kx^2 = 0, \text{ and } x = 0, \text{ or } \frac{2}{3}r.$$

$x = 0$ has no physical significance, but for $x = \frac{2}{3}r$, v will be a maximum. One substance must therefore be present in twice the quantity (by volume) of the other for the reaction to proceed with the maximum velocity in a trimolecular reaction, and conversely, a reaction which proceeds with the maximum velocity at any given temperature when two volumes of one substance react with one of another must be one of the

[1] Greater radiation from the mixtures containing a large amount of hydrogen cannot be the cause as the mixture $2H_2 + O_2 + 4N_2$ among others shows the same relative behavior.

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third order. The reaction between carbon monoxide and oxygen where the maximum velocity (or lowest ignition temperature) is shown by the mixture $2CO + O_2$ is trimolecular, and the reaction between hydrogen and oxygen where the maximum velocity is shown not by the mixture $2H_2 + O_2$ but by the mixture $H_2 + O_2$ cannot be trimolecular.

The value of v at the ignition temperature for the mixture $2CO + O_2$ is $v = k\left(\frac{2r}{3}\right)^2\frac{r}{3} = \frac{4kr^3}{27}$. If inert gas is added to take up one-fourth of the volume, the velocity will be $v_1 = k_1\left(\frac{r}{2}\right)^2\frac{r}{4} = \frac{k_1r^3}{16}$, or at the ignition temperature of the first mixture, $k_1 = k$, and $\frac{v_1}{v} = \frac{27}{64}$. At the same temperature the velocity of reaction of the mixture $2CO + O_2 + N_2$ will be $\frac{27}{64}$ as great as that of the mixture $2CO + O_2$. Experimentally (equation (b)) it was found that a rise in temperature of 40° would cause the same velocity for the former mixture as for the latter, ignition being brought about then in both cases. For a 10° rise, therefore, between the limits of the ignition temperatures of these mixtures, the temperature coefficient is $\sqrt[4]{\frac{64}{27}} = 1.24$. For other mixtures the following values are obtained:

	Temperature coefficient per 10° rise	Between the temperature limits
($2CO + O_2$ and $2CO + O_2 + N_2$)	1.24	874. — 917.
($2CO + O_2 + N_2$ and $2CO + O_2 + 2N_2$)	1.18	917. — 958.
($2CO + O_2 + 2N_2$ and $2CO + O_2 + 3N_2$)	1.14	958. — 1000 (approx.)

The temperature coefficient decreases from 1.24 at about 900° to 1.14 at about 1000°, values which are very close to those obtained for the reaction between hydrogen and oxygen.

The attempt to apply these principles to mixtures of carbon monoxide and oxygen containing an excess of one of the active constituents will not be made here, as there are some apparently contradictory and inexplicable features in the ignition temperatures of these mixtures. For instance, the ignition temperature of the mixture $6CO + O_2$ is 994°, but replacing part of the carbon monoxide by nitrogen lowers the ignition temperature so that for the mixture $4CO + O_2 + 2N_2$ the value 940° is found. An excess of carbon monoxide above a certain amount has a negative catalyzing effect.

Bodenstein and Ohlmer[1] found the same effect on measuring the velocity of the reaction on quartz surfaces between carbon monoxide and oxygen, an excess of carbon monoxide retarding the reaction. As shown

[1] Z. phys. Chem., 53, 166.

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above, hydrogen appears to exert a similar negative catalyzing effect, but not as pronounced, on the reaction between hydrogen and oxygen.

Conclusions.

The ignition temperatures of mixtures of:

Hydrogen and oxygen, carbon monoxide and oxygen, hydrogen, oxygen and nitrogen, carbon monoxide, oxygen and nitrogen, and hydrogen, carbon monoxide and oxygen, were determined by the "adiabatic compression method," and the possible sources of error fully discussed.

It is shown how the ignition temperature of any gaseous mixture containing hydrogen, carbon monoxide, oxygen, and an inert gas, may be calculated.

The reaction between hydrogen and oxygen is shown to be bimolecular and between carbon monoxide and oxygen, trimolecular.

The velocity coefficient per 10° rise in temperature is calculated to be 1.31 at about 800° and 1.13 at about 900° for the reaction between hydrogen and oxygen, and 1.24 at about 900° and 1.14 at about 1000° for the reaction between carbon monoxide and oxygen.

The reactions between hydrogen and oxygen in the presence of an excess of hydrogen and between carbon monoxide and oxygen in the presence of an excess of carbon monoxide do not follow the simple laws of chemical kinetics.

LABORATORY OF PHYSICAL CHEMISTRY,
July, 1907.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 18.]

SOLUTIONS OF METALS IN NON-METALLIC SOLVENTS; I. GENERAL PROPERTIES OF SOLUTIONS OF METALS IN LIQUID AMMONIA.

BY CHARLES A. KRAUS.

Received September 11th, 1907.

INTRODUCTION.

The present investigation was undertaken for the purpose of obtaining evidence regarding the nature of the process of electrical conduction in metals. In order to indicate in what respect the solutions of metals in non-metallic solvents are of especial importance in connection with the problem of metallic conduction, it will be necessary to consider, briefly, the experimental aspects of this problem, particulary in relation to the methods to be employed in its attack.

To account for the electromagnetic properties of metals, especially for the relation betweeu electrical and thermal conduction, the electron theory of metallic conduction has been advanced. According to this theory, the passage of electricity through a metallic conductor is effected by the movement of charged carriers, the electrons, whose mass, relative to charge, is many times smaller than that of the hydrogen ion, and whose

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state, when present in metallic substances, resembles that of a gaseous system. In the light of this theory, the process of metallic conduction is in many respects similar to that of electrolytic conduction; and it should be possible to obtain direct evidence proving the existence of the carriers as well as determining their nature. With regard to their external manifestations, however, the two processes differ widely; for, while in electrolytic conductors the current is accompanied by a transport of matter, in matallic conductors material effects appear to be altogether wanting. Herein lies an obstacle which has thus far checked all efforts to prove, directly, the existence of charged carriers in metals. That material effects are quite absent, however, has by no means been demonstrated; the order of magnitude of these effects may merely be much smaller than that observed in the case of electrolytic conduction. To give a definite answer to this question, it will not only be found necessary to employ highly refined methods for detecting the changes sought for, but the system to be investigated will have to be selected with a view to obtaining that best adapted to the problem in hand.

Under the most favorable conditions, however, it is doubtful whether the study of the conduction process in solids will lead to results immediately applicable in the solution of the problem of metallic conduction. Our knowledge of the solid state of matter, in general, is far too limited to enable us to determine the nature of the processes which are specifically involved when electricity passes through a metal. The study of the conduction process cannot be successfully carried out until the molecular state of the system has been established; even in the case of electrolytes the progress of investigation is governed by this condition. Only in the case of gaseous systems and certain simple types of liquid systems may the study of this process be undertaken with a measure of success.

It is highly probable that many results obtained in the study of ionized gases are in some degree applicable to the problem of metallic conduction. Their applicability, however, is restricted by the fact that ionized gases are not in a state of equilibrium, while the ionic concentrations are necessarily extremely small. On the other hand, gaseous systems which are normally in a conducting state, such as the vapors of the alkali metals, do not readily lend themselves to investigation.

The most advantageous conditions for the study of the problem of metallic conduction may be expected to exist in solutions of metals in inactive, non-conducting solvents. The solvent would here serve as a basis of reference with respect to which the state of the system might be determined, just as in the case of electrolytic solutions the presence of the solvent has made it possible to determine the nature of the conduction process in them. It may be expected that such solutions of metals will exhibit pronounced metallic properties when concentrated, and that, as

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the concentration diminishes, these properties will suffer modification, gradually approaching a limiting condition which is characteristic for solutions of this kind. As a class, the metals possess many striking properties in common whereby they are rather sharply distinguished from non-metallic substances. In solution, this community of properties should reappear, and the characteristic differences between metals and non-metals should manifest themselves in a corresponding divergence in the properties of their solutions. As is well known, the metals conduct the electrical current with remarkable facility, and it may be expected that in their solutions they will retain this property in some degree. If, then, the process of metallic conduction consists in a motion of charged carriers as the electron-theory postulates, in dilute solutions of metals, where complicating auxiliary phenomena are largely eliminated owing to the highly attenuated state of the dissolved substance, any fundamental relationships between the processes of electrolytic and metallic conduction should be clearly brought out.

It is the purpose of this investigation to show that solutions of metals in non-metallic solvents exist, and that such solutions exhibit well defined and characteristic properties. Moreover, the molecular state of the more dilute solutions will be determined, and it will be shown in what respects the process of conduction therein is related to the process of conduction in electrolytic solutions. Finally, an attempt will be made to determine to what extent the process of conduction has undergone modification in consequence of dilution.

That the alkali metals are soluble in liquid ammonia has long been known, and at various times the metallic nature of these solutions has been conjectured. Their significance, however, in relation to the study of the state of metallic substances, particularly to that of the metallic elements, has never been fully realized. It is in this connection that the writer was led to take up the investigation of solutions of metals, and, as will appear in the sequel, the expectation that these solutions would furnish a means of attacking the problem of metallic conduction has been amply justified. At the time that this investigation was undertaken, almost no quantitative data relating to the physico-chemical properties of the metal solutions in liquid ammonia were available, and even some of the more qualitative facts were not established. It was necessary, therefore, to make an exhaustive study of these solutions. The prosecution of this investigation has made great demands on both time and patience, and progress has at times seemed painfully slow. Not only was it necessary to develop an extensive technique, in order to manipulate successfully an extremely reactive solute and a highly volatile solvent, but the number of experiments had to be multiplied many times in order to exclude certain

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disturbing factors which have their origin in a slow reaction taking place between the two components.

Although in certain directions, this investigation is as yet incomplete, the accumulation of material makes it desirable to publish the results obtained. Because of the length and comparatively independant nature of the different investigations involved in this problem, it seems best to present them separately. The lack of existing data on which a more precise study of the physical properties of metal solutions in ammonia could be founded, made it necessary to do much preliminary work of a qualitative character. The greater portion of these results will be embodied in the first two papers, of which the first will deal with some of the general properties of the solutions in question, and the second with the question of the formation of compounds between ammonia and metals. The third paper will treat of the molecular weight of sodium dissolved in liquid ammonia; the fourth and fifth papers will embrace a preliminary survey of the electrical properties, while succeeding papers will treat of these more in detail. Although the chief interest centers about the conduction process in these solutions, many of the results obtained have a bearing on other questions. These will be treated incidentally as they appear in this discussion. In view of the nature of the subject, the general discussion of the results will be reserved until a fairly complete presentation of the experimental data has been made.

In the course of this investigation of solutions of metals, the writer has been led to search for other metallic systems possessing properties such that their study might yield results throwing light on those molecular conditions which impose upon a body its metallic properties. Several such systems have been found. One of these is the series of solutions formed between sulphur and tellurium and another is a series of electropositive metallo-organic groups, namely: CH_3Hg, C_2H_5Hg, and C_3H_7Hg, which have been obtained in a free state and which exhibit distinct metallic properties. Although a detailed study of these systems, particularly the latter, is attended with serious experimental difficulties, it is hoped that an outline of their properties may shortly be given.

The greater portion of this investigation has been carried out in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology during the past three years. It is with much pleasure that the writer avails himself of this opportunity of acknowledging his indebtedness to Professor A. A. Noyes, both for the use of the facilities of the Research Laboratory, and for that interest which has made it possible to carry this investigation to a successful conclusion.

General Properties of Solutions of Metals in Liquid Ammonia.

Solubility Relations.

According to the literature, the following metals are soluble in liquid

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ammonia, namely: Sodium, potassium,[1] lithium,[2] rubidium, caesium,[3] calcium,[4] barium,[5] and strontium.[6] Magnesium is likewise somewhat soluble,[7] while lithium[8] and caesium[9] are soluble in methylamine.

Since different solutions exhibit different degrees of stability, it was found desirable to extend, as far as possible, the number of solutions that may be formed. In determining whether or not a metal is soluble, it is necessary to have a dry solvent and a clean metallic surface. In all doubtful cases the metal was melted in the solvent and while in the act of solidifying, the containing tube was shaken vigorously. In this way the metal was obtained in the form of very small globules. This process was repeated a number of times, after which the tube was allowed to stand undisturbed for some months. Lithium was thus found to be soluble in ethylamine, although less so than in methylamine. In propylamine, lithium is insoluble, as was shown by precipitating the metal electrolytically from a solution of its salt. Potassium dissolves rather slowly in ethylenediamine, giving a solution which does not possess sufficient stability to make it valuable for experimental purposes. Other metals have not been investigated in this solvent. Sodium and potassium are insoluble in ethylamine; and sodium, potassium and, lithium are insoluble in secondary and tertiary amines. According to Moissan, sodium and potassium are insoluble in methylamine[10] which is free from ammonia.

Another series of solutions possessing great interest, has been obtained by Palmaer[11] in electrolyzing solutions of tetra-alkylammonium salts in ammonia. The blue solution, which under these circumstances is formed at the cathode, is ascribed to the presence of the free electropositive group. In view of the characteristic nature of the color of the metal solutions in ammonia, it seems highly probable that Palmaer's interpretation is correct. These results of Palmaer I have been able to verify, and in addition, it has been found that tetrapropylammonium salts exhibit a behavior similar to that of the methyl and ethyl derivatives, while with

[1] Weyl, Ann. Physik., 121, 601 (1864).

[2] Seely, Chem. News, 23, 169 (1871).

[3] Moissan, Compt. rend., 136, 1177 (1903).

[4] Moissan, Ibid., 127, 685 (1898).

[5] Guntz, Ibid., 133, 874 (1901); Mentrel, Ibid., 135, 740 (1902).

[6] Guntz, Ibid., 133, 1209 (1901).

[7] Seely states that magnesium is insoluble. However, according to observations made by Dr. F. G. Cottrell, of the University of California, and communicated to the writer by letter, this metal dissolves in ammonia if precautions are taken to have a clean metallic surface in contact with the pure solvent.

[8] Moissan, Compt. rend., 128, 26 (1899).

[9] Rengade, Ibid., 140, 246 (1905).

[10] Ibid., 128, 26 (1899).

[11] Z. Elektrochem., 8, 729 (1902).

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the amyl derivative a blue solution could not be obtained. Because of their lack of stability, these solutions could not be further studied.

The blue colored halide salts of sodium and potassium may likewise be mentioned here. These salts are formed by the action of strong Röntgen rays[1] and by the action of the alkali metal vapors on their halide salts at higher temperatures,[2] while a blue sodium salt occurs in nature. The color of these salts has been ascribed to the formation of a subhalide salt,[3] to the formation of a solid solution of the metal in the salt,[4] and finally to the presence of ultramicroscopic particles of the free metal.[5] That the color of these salts is not due to the presence of a subhalide is indicated by the fact that sodium chloride crystallizes from a solution of sodium in ammonia as a colorless salt.[6] While in some cases, at least, the color is due to the presence of particles of free metal, it is possible that, under certain conditions, solid solutions may be formed. In preparing the amides of the alkali metals by passing ammonia gas over the fused metals, a blue colored solution is formed which loses its color under the action of an excess of ammonia. This color has been ascribed by Titherly[7] to the formation of a solution of the metal in the fused amide.

Solutions of Metallic Compounds.

In addition to the solutions of the elementary metals which have just been described, a few instances are known where metallic compounds dissolve in liquid ammonia. Joannis[8] has shown that lead dissolves in ammonia solutions of sodium, provided the latter metal is not present in excess; in solution, two atoms of lead are present for one atom of sodium. As with solutions of the elementary metals, at a given vapor pressure of ammonia, metal is precipitated, redissolving on addition of ammonia. Lead, I find, is likewise soluble in solutions of potassium, while tin is soluble in solutions of sodium. The lead solutions have a greenish color while the tin solutions exhibit a red color. Both are very stable, as is shown by the fact that such solutions have remained sealed up for several years without losing their characteristic color. According to Lebeau[9] the compound Li_3Sb is soluble in ammonia.

From a brief preliminary study which I have carried out, it appears that the ammonia solutions of metallic compounds exhibit properties

[1] Goldstein, Ann. Physik., **59**, 371 (1895).
[2] Giesel, Ber., **30**, 156 (1897).
[3] Wiedemann and Schmidt, Ann. Physik., **54**, 622 (1895).
[4] Elster and Geitel, Ibid., **59**, 487 (1896).
[5] Siedentopf, Physik. Z., **6**, 855 (1905); Z. Elektrochem., **12**, 635 (1906).
[6] Cf. Joannis, Compt. rend., **112**, 392 (1891).
[7] J. Chem. Soc., **65**, 508 (1894); **71**, 469 (1897).
[8] Compt. rend, **113**, 795 (1891).
[9] Ibid., **134** (1902).

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very different from those of solutions of the elementary metals. They exhibit polarization, as was shown by the fact that in resistance measurements, in which a telephone was used, a very poor minimum was obtained with bright platinum electrodes, whereas solutions of the elementary metals, whether dilute or concentrated, give an excellent minimum even when extremely small electrodes are employed. The conductivity-temperature curves for these solutions are similar to those of ordinary electrolytes[1], in which respect, again, they differ from solutions of sodium, as will be seen from results appearing in a subsequent paper.

In passing a current between lead electrodes in a solution of the sodium-lead compound, it was found that lead is precipitated on the anode and dissolved at the cathode, as appears from the following results: With a current of 0.106 ampere flowing for 54 minutes there was found a gain of 1.432 g. of lead at the anode and a loss of 1.473 g. at the cathode. Assuming two gram-atoms of lead per equivalent of electricity, the calculated value is 1.473 g. In another experiment with a current of 0.106 ampere flowing for 40 minutes the loss and gain were found to be 1.075 g. and 1.085 g. of lead respectively; calculated 1.091 g. Especial care was not taken to exclude loss of material nor was the current measured with an accuracy of more than 1 per cent. The differences between the observed and calculated values are doubtless due to errors of this character. From these results it appears that for every equivalent of electricity, two gram-atoms of lead are transferred from the cathode to the anode. It is probable, therefore, that in solution the ions, Na^+ and Pb_2^-, act as carriers for the current. That ammonia may be associated with either or both of these ions is by no means excluded.[2] If such should be the case the part played by the ammonia may be expected to be similar to that which the solvent plays in connection with the ions of ordinary salts.

On electrolyzing a solution of sodium chloride with a lead cathode, and an anode of sodium amalgam, the compound is formed at the cathode, as is shown by the color change. Also, on adding lead iodide to a solution of metallic sodium, the compound is formed, provided the lead salt is not added in excess of that required to just form the compound. Solutions of the compound of lead and sodium are stable in the presence of sodium chloride; with ammonium chloride a metallic precipitate results, along with evolution of gas, doubtless hydrogen, The addition of a lead salt precipitates a spongy metal, presumably metallic lead. In general, the addition of the salt of a metal causes a metallic precipitate which contains both lead and the metal in question. All these facts harmonize with the assumption that the ions Na^+ and Pb_2^- are present in solution.

[1] Franklin and Kraus, Am. Ch. J., 24, 83 (1900).

[2] Cf. Joannis, loc. cit.

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Since these solutions are purely electrolytic conductors, they are not of special significance in connection with the main purpose of the present investigation.[1] They are, however, of great interest in showing that under proper conditions there may be present in solution, a kind of ions otherwise unknown, namely: anions composed of metallic elements. Furthermore, if the solutions of the sodium-lead compound in ammonia may be looked upon as a solution of the metallic compound $NaPb_2$, it follows that this compound possesses polar properties; in other words, this metallic compound may be looked upon as being of the nature of a salt. Conclusive evidence regarding this point can be obtained only by a detailed study of the properties of these solutions.

The Solubility Diagram for Sodium in Ammonia.

The solubility of the metals in ammonia is, on the whole, very great. According to Ruff and Geisel[2] one atom of sodium, potassium and lithium dissolves in 5.87, 4.74 and 3.87 molecules of ammonia respectively, at 0°. The solubility of potassium increases slightly with the temperature, that of sodium decreases, while that of lithium remains sensibly constant over a temperature range of 100°.

The complete solubility diagram of the metals in ammonia is not known. The behavior of sodium, however, has been studied sufficiently to make it possible to predict the general form of the curve for the more dilute solutions. This curve is represented in Figure 1, in which the continuous lines represent actual determinations, while the broken lines are conjectured, not being based on actual determinations. The points on the branch AB represent solubilities of sodium in ammonia as determined by Ruff and Geisel.[3] The points on the branch DE were determined approximately by the writer from conductivity data, while the point F is the freezing point of pure ammonia.

The curve FE represents the composition of solutions in equilibrium with solid ammonia. On the curve CDE two liquid phases are in equilibrium, namely: solutions of concentration *d*-*c* with solutions of concentration *d*-*e*. On BC, again, solutions of concentration *b*-*c* are in equilibrium with solid ammonia; and finally, on BA, solutions are in equilibrium with solid sodium. On cooling a solution whose composition lies between *c* and *e*, separation takes place into two liquid phases, for which D is the point of complete miscibility. This point has not been determined, but its temperature is known to lie below —33° and and above —56°, probably not far from —50°, while the critical compo-

[1] Since writing the above, I have had occasion to work with more concentrated solutions of the sodium-lead compound. It appears that very concentrated solutions of this compound possess marked metallic properties, although by no means as strong as those of solutions of the elementary metals. It seems likely, therefore, that these solutions of metallic compounds will have to be included in this investigation.

[2] Ber., 39, 828 (1906).

[3] Loc. cit.

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sition probably lies considerably below 10 per cent. (by formula weight) of sodium. The point E has not been determined but, since this solu-

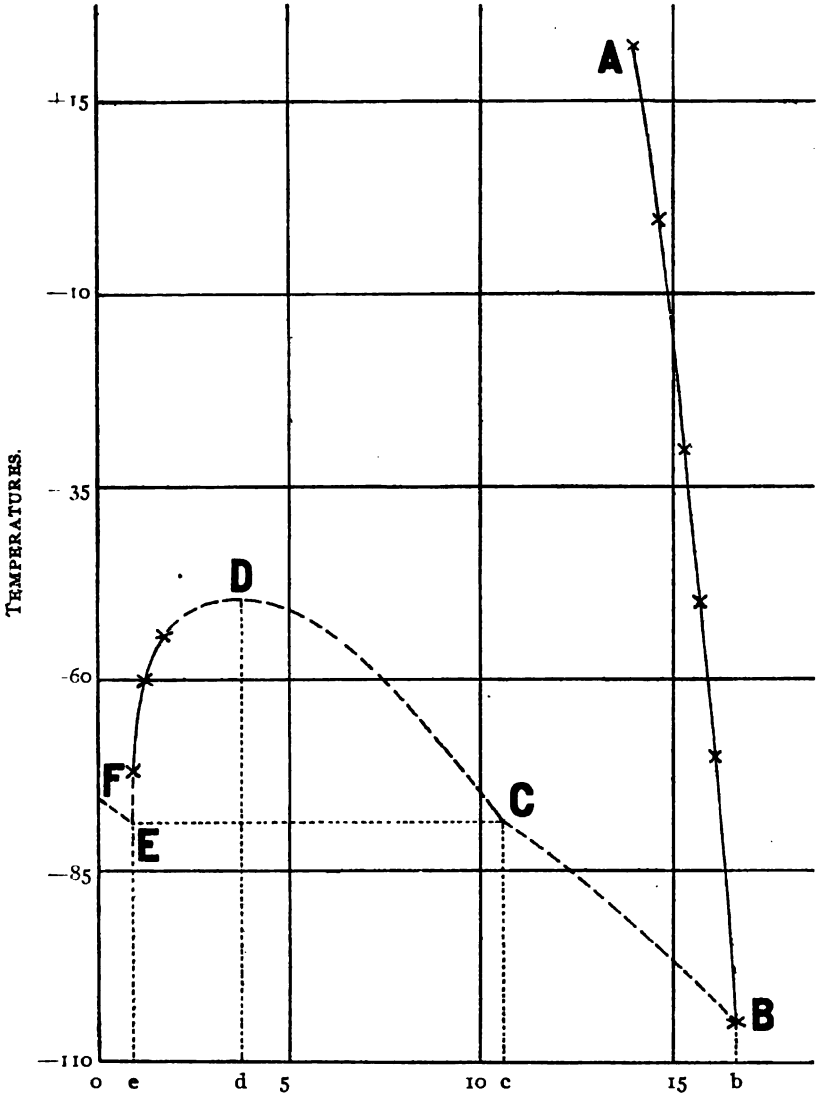


FIGURE 1.—Solubility Diagram for Sodium in Ammonia.

tion is comparatively dilute, its freezing point can not lie much below the normal freezing point of ammonia.

The separation of the sodium solution into two liquid phases is a most striking phenomenon. The more dilute solution, dark blue in color, appears at the bottom ; while above it appears the more concen-

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trated solution, presenting a characteristic bronze colored metallic appearance. The fact that both series of solutions contain less than 15 per cent. of sodium is very remarkable; it serves well to illustrate how rapidly the properties of these solutions change with concentration. These changes are of an order of magnitude not met with in the case of any solutions hitherto investigated; the actual magnitude of the changes involved will appear later when the more detailed investigations come up for discussion.

It would be interesting to extend the curve AB to the melting point of sodium. Since this point lies near 96° and the solubility of sodium in ammonia at 22° is decreasing with the temperature, it seems improbable that the curve AB will reach the melting point of sodium without exhibiting a maximum. If such is the case, a second series of partially miscible liquid phases must exist[1], containing larger percentages of metal. Of course, a compound may make its appearance and change the form of the curve. Experiments at higher temperatures should lead to valuable results.

Whether or not other metals exhibit the same properties as sodium can not be predicted with certainty. However, from certain observations recorded by Moissan[2] and Mentrel[3], it is probable that solutions of calcium and barium will be found to behave like those of sodium[4].

Mixed Solvents.

The first observations on the solubility of metals in mixed solvents are due to Moissan[5], who showed that lithium is soluble in methylamine which has been diluted with ether. From a qualitative study which I have made of a considerable number of solvents it may be concluded that, in general, the alkali metals are soluble in any inactive solvent containing a considerable quantity of ammonia. If the solvent is miscible with ammonia in all proportions and sufficient metal is added, two liquid phases usually result. One of these consists chiefly of ammonia and, retaining nearly all the metal, possesses a decided metallic appearance, while the other consists chiefly of the inactive solvent and, containing but little metal, appears blue. If the neutral solvent possesses a very limited solubility for ammonia, as for example toluene, the solutions of

[1] This view gains some support from recent investigations which I have carried out with alloys of sodium and potassium. From these it appears that ammonia gas is somewhat soluble in the liquid alloy of the two metals. The details will appear later.

[2] Compt. rend., 127, 685 (1898).

[3] Ibid., 135, 740 (1902).

[4] It has since been found that calcium behaves in a manner similar to that of sodium. In this case, however, the point of complete miscibility must lie much above room temperatures. The concentration of the more dilute phase is in the neighborhood of 1/10 molal at −33°.

[5] Compt. rend., 128, 30 (1899).

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the metal are very dilute; with other solvents, such as the amines, a very considerable solubility for the metal may result.

The addition of a salt of a metal to a solution of the metal itself in ammonia results in a depression of the solubility of the metal; in fact, it usually results in the production of a second liquid phase if sufficient metal is present to cause saturation of the dilute solution. Thus, on adding sodium chloride, in excess, to a strong solution of sodium, two liquid phases result, one of metallic appearance, containing most of the metal; the other of a blue color, more dilute in metal, and probably containing the greater proportion of salt.

Stability.

The rate of reaction between ammonia and the dissolved metal, whereby the corresponding amide is formed[1] together with hydrogen gas, is of great importance from an experimental standpoint, since the presence of the amide necessarily affects the results of all quantitative measurements. The stability of the solutions increases in the order: potassium, calcium, lithium, sodium. The reaction, however, is one that is catalyzed by many substances[2]. As follows from results to appear later, it is probable that the metallic oxides and hydroxides exert a catalytic action, and for this reason some change may result in the order of stability when pure substances are employed. The necessity for excluding catalytic agents greatly increases the experimental difficulties in studying the metal solutions.

Influence of Pressure on Stability.

According to Joannis,[3] the rate at which hydrogen is evolved in a sealed tube containing a solution of sodium decreases with time. This behavior he ascribes to the influence of the increasing hydrogen pressure on the rate of reaction. Such an influence is scarcely credible; nevertheless, its possibility and the fact that it would afford a means of decreasing the rate of reaction at higher temperatures, is of so great a practical importance that it seemed worth while to investigate the question more carefully.

The apparatus employed is outlined in Figure 2. The pressure was measured by means of a Crosby gauge G, graduated in pounds and reading to as high as 400 pounds. This gauge was specially constructed for use with liquified gases and was very reliable. The sodium solution was contained in the tube C about 15 centimeters long and of one centimeter diameter. The apparatus was provided with a mercury injector I, by means of which mercury could be introduced into, or withdrawn from the system. The gauge and connecting tube, as far as A, were

[1] Joannis, Compt. rend., 112, 392 (1891).

[2] Compare Joannis, loc. cit.; Franklin, this Journal, 27, 831 (1905).

[3] Loc. cit.

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filled with oil; the connecting tube D and the tube AB were filled with mercury, and by means of the injector the mercury was always main-

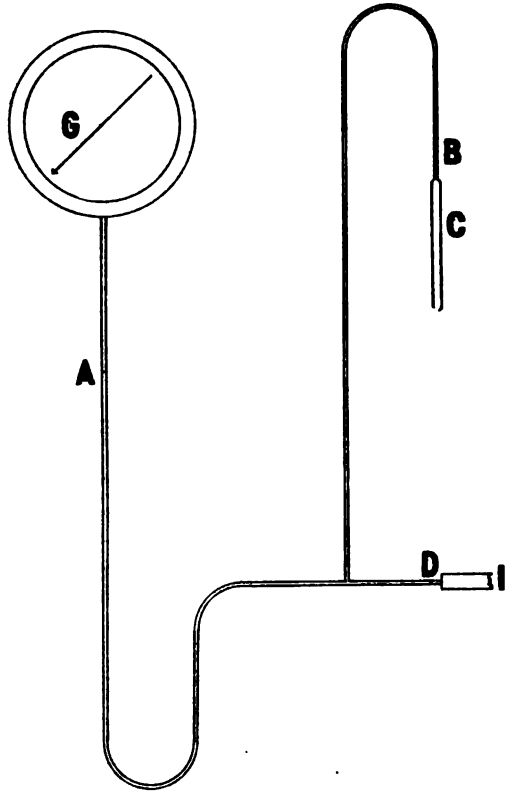


FIGURE 2.—Apparatus Employed in Measuring the Rate of Evolution of Hydrogen from a Sodium Solution. Dimension Reduced in Ratio of 10:1.

tained at the fixed point B in order to keep the vapor volume in the tube C constant.

Approximately 1.5 g. of pure sodium were introduced into the tube C. This was accomplished by exhausting the apparatus and forcing melted sodium through a glass wool filter by means of a small pressure of pure ammonia gas. The tube in which the sodium was melted and filtered was attached to the tube C and sealed off as soon as the metal had been forced over. A sufficient quantity of pure dry ammonia[1] to dissolve all the sodium was distilled into C through a connecting tube (not shown in the figure) which was later sealed off. A portion of this ammonia was again evaporated, leaving 1.5 cubic centimeters in the tube. The purpose of this operation was to leave the metal in a less compact form

[1] In all cases where quantitative results have been obtained, pure ammonia has been employed, the method of purification being that of Franklin and Kraus, in which the solvent is distilled from a solution of sodium or other active metal Am. Ch. J., 23, 284 (1900).

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in order to insure equilibrium conditions. Since excess of metal was always present, the vapor pressure of the solution necessarily remained constant. After sealing up the apparatus the tube C was placed in a thermostat and maintained at a temperature of 36° within a few hundredths of a degree. The results are represented graphically in Figure 3. Similar results were obtained in a duplicate experiment.

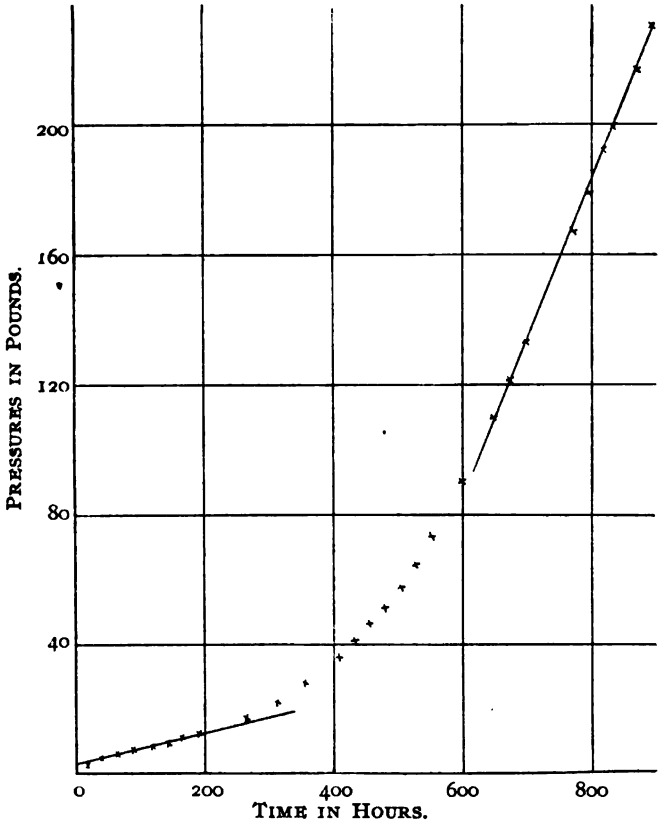


FIGURE 3.—Plot, Showing Rate of Evolution of Hydrogen from a Sodium Solution in Ammonia.

It will be seen from the plot that for the first 250 hours, the pressure increases at a nearly constant rate, but that during the next 400 hours, a great acceleration takes place, after which the rate again becomes nearly constant. Ultimately, of course, the rate of evolution of hydrogen must decrease again owing to diminution in the amount of the reacting constituents. In this experiment the ammonia used up did not exceed 25 per cent. of the initial quantity.

It is probable that this observed acceleration of the rate of the reaction, $Na + NH_3 = NaNH_2 + \frac{1}{2}H_2$, is due to the catalytic action of the solid product, sodamide, which soon begins to precipitate from the solution

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on account of its small solubility. There is no indication, therefore, that an increase in the concentration of hydrogen in contact with a sodium solution causes a decrease in the rate of reaction between sodium and ammonia.

Some Physical Properties.

As is well known, concentrated solutions of the metals possess metallic luster, somewhat of a bronze color. The color in question differs but slightly for different metals although the appearance of yellow tints is noticeable in the case of calcium. More dilute solutions, beginning at about 2 or 3 normal, show no metallic luster, but possess a very characteristic deep blue color. In thin films, the concentrated solutions likewise appear blue in transmitted light; but even for the blue rays the absorption is very great. A solution of sodium in ammonia containing 1/250 gram-atom of metal per liter, just allows the filament of a 16 candle-power lamp to be distinguished through a thickness of 1 centimeter. The absorptive power of potassium in ammonia is practically identical with that of sodium.

On evaporating a solution of metal in ammonia, the vapor pressure of the solvent decreases with increasing concentration of the solution until a saturated solution is obtained, when the pressure remains constant until all the ammonia has been vaporized and free metal remains behind. The change of this pressure with temperature has been determined by Joannis[1] for solutions of sodium and potassium. The temperatures at which the different metals are attacked by ammonia vapor at atmospheric pressure have been determined by Moissan[2] as follows: lithium, 70°; sodium, —20°; potassium, —2°; rubidium, —3°; caesium, 40°; calcium, 20°[3].

The heats of formation of saturated solutions of sodium and potassium from solid metal and ammonia vapor have been determined by Joannis[4], who found 5.2 and 6.4 calories per gram-atom of metal, respectively. These values are in good agreement with those deduced thermodynamically from the pressure-temperature curves. The amount of heat evolved in dissolving the metals in liquid ammonia is very small indeed, for the heat of vaporization of ammonia at its boiling point is 5.6 calories,[5] thus indicating that the forces coming into play in the process of solution are extremely feeble.

Summary.

The behavior of non-metallic solvents is investigated with respect to

[1] Ann. chim. phys., 7, 49 (1906)

[2] Compt. rend., 127, 685 (1898); 136, 1177 (1903).

[3] It might be inferred from this that at 20°, the equilibrium pressure in the case of calcium is equal to one atmosphere. As will appear from results to be communicated in the next paper, such is not the case. The discrepancy is doubtless due to the slowness with which equilibrium establishes itself.

[4] Compt. rend., 109, 965 (1889).

[5] Franklin and Kraus, Am. Ch. J., 21, 12 (1899).

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their power of dissolving metals. Lithium is found to be soluble in ethylamine and potassium in ethylenediamine. In the higher members of the primary amines as well as in the secondary and tertiary amines, the alkali metals are insoluble. The behavior of mixed solvents has also been studied. As a rule, the alkali metals are soluble in any inactive solvent containing considerable ammonia, and the solubility is the lower the smaller the amount of ammonia present. If sufficient metal be added to a solvent containing ammonia, the system, in general, separates into two liquid phases which differ markedly in their content of metal as well as in appearance. A similar separation takes place when salt is added to a metal solution in ammonia.

Dilute solutions of the compound $NaPb_3$ are shown to be electrolytic in nature. An investigation of the products of electrolysis of these solutions indicates that the ions Na^+ and Pb_3^- are present, since two gram-atoms of lead are transferred from the cathode to the anode for one equivalent of electricity. A number of reactions in which this compound takes part have been studied and the results are in accord with this hypothesis. Tin likewise is soluble in an ammonia solution of sodium.

The form of the solubility curve for sodium in ammonia is in part given, in part conjectured from indirect observations. It is shown that over a limited range of concentration two solutions of sodium coexist. Both contain less than 15 per cent. of sodium (according to the formula weight), and their critical point of solution lies in the neighborhood of —50° and 10 per cent. of sodium.

A study is made of the rate of the reaction, $Na + NH_3 = NaNH_2 + \frac{1}{2}H_2$ as it takes place in a sealed tube at different times. After an initial period of some days, during which the rate of reaction is nearly constant, a great acceleration is observed. This acceleration is probably due to the catalytic action of solid sodamide, which begins to precipitate out after a time. Contrary to the observations of Joannis, there is no indication that the rate of the above reaction is retarded by the presence of hydrogen gas.

Boston, September 7, 1907.

THE CATALYSIS BY ACIDS AND BASES OF THE MUTAROTATION OF GLUCOSE.

By C. S. Hudson.

Received July 23, 1907.

The mutarotation[1] of aqueous solutions of glucose follows the formula of a monomolecular reaction. As is well known its rate is enormously

[1] This term which has been introduced by T. M. Lowry is here adopted in preference to the words "birotation" and "multirotation," as a name for the slow change in the power of rotating polarized light that is shown by freshly prepared solutions of glucose and other related sugars.

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influenced by the temperature of the solution and by the presence in it of acids and bases, but on the other hand no strong accelerative action is exerted by neutral substances which do not undergo hydrolysis in solution. Acids and bases are also specific catalyzers of the mutarotation of milk-sugar, while neutral substances are in this case also without comparable influence. This fact that only the hydrogen and hydroxyl ions are strong catalyzers of the mutarotation of these two sugars deserves careful study because such a peculiar specific catalytic action is probably intimately related with the causes of the mutarotation. The present article presents measurements that were undertaken in order to determine what relation exists between the concentration of the catalyzing agent and the amount of its accelerative action. These measurements show that the relationship over the whole range of acid and alkaline solutions and pure water can be expressed by a simple formula which can also be derived theoretically from simple assumptions.

Measurement of the Rate of Mutarotation in Acid Solutions Near 25°.

The following experiments were made with a polariscope sensitive to 1/20 degree using a jacketed observation tube 20 cm. long which was kept at a constant temperature of 24.°7 by a stream of water supplied from a large thermostat. The solutions were prepared by dissolving four grams of anhydrous crystalline *d*-glucose, of the best quality that is supplied by Kahlbaum, in twenty cubic centimeters of distilled water or hydrochloric acid solutions of different strengths, filtering, and observing the angle of rotation at intervals during about one hour. The first measurements were taken ten minutes or in some cases five, after the glucose was mixed with the water, and the final constant rotation was obtained by adding two or three drops of strong ammonia to the solution in the polariscope tube. For all the concentrations of acid that were used duplicate experiments were made and the agreement was uniformly good; the following table contains the results of all the experiments that were performed. The time is expressed in minutes, the reading of the polariscope in degrees, and the velocity-constant of the reaction, k, is calculated from the usual formula, $k = \frac{1}{t} \log. \frac{r_0 - r_\infty}{r - r_\infty}$, using common logarithms.

It is apparent from the data given in the following table that the rate and the acid concentration bear a linear relation to each other and that a minimum rate occurs in weakly acid solutions. Although this minimum rate is difficult to detect with certainty, its presence can hardly be doubted because two other observers, Trey[1] and Lowry[2], have also found that the rate is

[1] Trey, Z. physik. Chem., 22, 443, 448 (1897). See also Osaka, Z. physik. Chem., 35, 702 (1900).

[2] Lowry, J. Chem. Soc., 83, 1314 (1903).

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TABLE I

RATE OF MUTAROTATION OF GLUCOSE IN HYDROCHLORIC ACID SOLUTIONS AT 24.°7.

No.	Concentration HCl (mol./liter)	Reading at time 0	5	15	25	35	45	60	∞		k
1	Distilled	34.2	32.4	29.2	27.0	25.3	24.0	22.5	18.5	0.0106	0.0106
2	Water	32.8	30.8	28.4	25.8	24.2	22.8	21.5	17.7	0.0107	
3	0.001	33.9	32.2	29.3	26.7	25.1	23.7	22.2	18.0	0.0099	0.0098
4	0.001	32.7	30.8	28.2	26.2	24.4	22.8	21.2	17.2	0.0098	
5	0.005	32.5	30.6	27.8	25.3	23.6	22.2	20.8	17.5	0.0112	0.0112
6	0.005	32.6	30.7	27.6	25.4	23.6	22.0	20.7	17.4	0.0113	
7	0.01	32.4	30.4	27.4	24.8	23.1	21.5	20.2	17.3	0.0120	0.0121
8	0.01	33.2	31.2	28.0	25.5	23.6	22.2	20.8	18.0	0.0122	
	time	0	5	10	15	20	25	30	∞		
9	0.03	32.4	29.7	27.3	25.4	23.8	22.7	21.8	16.7	0.0168	0.0169
10	0.03	31.8	29.3	26.8	24.9	23.5	22.3	21.3	16.6	0.0170	
11	0.06	33.7	29.8	26.8	24.7	22.8	21.5	20.7	17.7	0.0244	0.0253
12	0.06	34.7	30.6	27.3	25.2	23.7	22.3	21.5	18.8	0.0262	
13	0.10	32.3	27.4	23.8	21.7	20.3	19.3	...	17.4	0.0357	0.0354
14	0.10	31.4	27.0	23.7	21.9	20.4	19.6	...	17.8	0.0352	

slightly less in weakly acid solutions than in pure water. This depression will be further considered later on.

A Formula for the Rate of Mutarotation in Acidic and Basic Solutions.

Osaka[1] has concluded from his measurements on the rate of mutarotation in acid and basic solutions that the rate is proportional to the concentration of hydroxyl ions in the basic solutions, but proportional to the square root of the concentration of the hydrogen ions in the acid solutions. While these conclusions express Osaka's measurements very well, it will be seen later in this article that they do not agree with those measurements of mine in acid solutions, which refer to concentrations outside the limits, 0.02 to 0.06 molal, studied by Osaka. And particularly they do not agree with the fact that a minimum rate occurs in weakly acid solutions. It is therefore necessary to seek some other expression for the rate in acid and alkaline solutions, one which shall take account especially of the depression of the rate in weakly acid solutions.

The simplest assumption regarding the influence of acids and bases on the rate of mutarotation is that both the hydrogen and hydroxyl ions accelerate the reaction and that the increase in the rate is proportional to the increase in concentration of the two kinds of ions. We should thus have $\Delta k = B\Delta(H^{\cdot}) + C\Delta(OH')$ and therefore $k = A + B(H^{\cdot}) + C(OH')$, where k is the rate of mutarotation in a solution which contains hydrogen and hydroxyl ions in the concentrations $(H^{\cdot})$ and (OH') respectively, and A, B, and C are constants. To obtain the values of these the preceding data on acid solutions have been used in connection with Osaka's measurements in basic solutions. Osaka's value for the rate in pure water is 0.0104, which agrees closely with the value that I have found, 0.0106, showing that the two sets of measurements were made at the same temperature, although slightly different values for it were

[1] Loc. cit.

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found, namely 25° and 24.°7. Using the rates of the preceding table (I), A is found to have the value 0.0096 and B, 0.258, and the measurements of Osaka on basic solutions shown in the following table (II) give 9750 as the value of C. The formula for the rate of mutarotation of glucose at 25° in pure water or in acid or basic solutions is, therefore,

$$k = 0.0096 + 0.258(H^{\cdot}) + 9750(OH').$$

In the following table are given the rates that Osaka has observed in basic solutions and those which I have found in acid solutions with the corresponding rate that is calculated from the above formula[1]. It will be seen that the formula expresses the rate over the complete range of concentration with an accuracy that is well within the errors of observation.

TABLE 2

COMPARISON OF OBSERVED AND CALCULATED RATES.

No.		Molal Concentration	Rate		Diff.	Observer
			Observed	Calculated		
1	Alkaline	0.0000022 (OH′)	0.0326	0.0310	+.0016	Osaka
2		0.0000033	0.0382	0.0418	—.0036	"
3		0.0000031	0.0446	0.0398	+.0048	"
4		0.0000044	0.0494	0.0486	+.0008	"
5		0.0000055	0.0640	0.0632	+.0008	"
6		0.0000066	0.0705	0.0739	—.0034	"
7	Pure Water	0.00000012	0.0106	0.0108	—.0002	Hudson
8	Acid	0.001 (H·)	0.0098	0.0099	—.0001	"
9		0.005	0.0112	0.0109	+.0003	"
10		0.01	0.0121	0.0122	—.0001	"
11		0.03	0.0169	0.0173	—.0004	"
12		0.06	0.0253	0.0250	+.0003	"
13		0.10	0.0354	0.0354	.0000	"

This table shows that there is a distinct depression of the rate in weakly acid solutions, its value for pure water being 0.0106 but for 0.001 HCl only 0.0098. The cause of this depression is obviously that the addition of small quantities of acid to pure water lowers the concentration of hydroxyl ions to nearly as great an extent as the increase in hydrogen ions and as the former are far stronger catalytic agents than the latter, the rate of mutarotation is necessarily decreased. But after the hydroxyl ions have been considerably reduced, further addition of acid accelerates the rate because the hydroxyl ions are now in such very small concentration that their further reduction is no longer of influence upon the rate. There must thus be a minimum rate in acid solutions; the concentration of acid which gives this minimum rate can be readily calculated from the formula above. Writing the first differential of k with respect to $(H^{\cdot})$ equal to zero and solving gives $(H^{\cdot}) = 2.3(10)^{-5}$ mols/liter. In an

[1] In calculating the rate in solutions from the above formula it is to be remembered that the product of the concentration of the hydrogen and hydroxyl ions is the dissociation-constant of water, $1.4(10)^{-14}$ at 25°. The equation can therefore be expressed in the form $k = 0.0096 + 0.258(H^{\cdot}) + \frac{(9750)(1.4)(10)^{-14}}{(H^{\cdot})}$, in which k and $(H^{\cdot})$ are the only variables.

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acid solution of this strength the rate is therefore minimum and has the value 0.0096, which is ten per cent. less than the rate for pure water. The concentration of acid which gives the same rate as pure water can likewise be found from the formula by writing $k = 0.0106$ and solving the resulting quadratic equation for $(H^{\cdot})$, which gives the value 0.004 mols/liter. We can therefore conclude that *acid solutions containing hydrogen ions in less strength than 0.004 molal retard the mutarotation of glucose, and those of greater strength accelerate it.* This conclusion from the above measurements is further supported by the previously mentioned observations of Trey and Lowry. Trey found that the rate was slightly depressed in one-tenth normal solutions of acetic and propionic acids, its value being 0.0082 in these solutions and 0.0087 in pure water. These acids are approximately one per cent. dissociated in tenth normal solution and the hydrogen ion concentration in them is therefore 0.001, which is within the region where a depressed rate of mutarotation is to be expected from the formula. Lowry observed a slight decrease of the rate in 0.001 and 0.0001 molal hydrochloric acid solutions, which are also within the region of depressed rates.

In conclusion the following table is given in support of the assumption that has been made in deriving the preceding formula, that the increase of the rate in acid solutions of appreciable strength is proportional to the increase in the concentration of the hydrogen ions. It will be seen from it that the numbers given in the fourth column agree as well as could be expected in such measurements, but on the other hand, the proportion factor given in the third column varies in a regular manner, showing that the rate is not proportional to the square root of the hydrogen ion concentration.

TABLE 3

RELATION BETWEEN THE ACID CONCENTRATION AND THE RATE.

Acid Concentration $(H^{\cdot})$	Rate k	$\frac{k}{(H^{\cdot})}$	$\frac{\Delta k}{\Delta(H^{\cdot})}$	Observer
0.001	0.0098	0.310		Hudson
0.0245	0.0172	0.110	0.315	Osaka
0.0323	0.0186	0.102	0.281	"
0.0480	0.0244	0.112	0.311	"
0.0633	0.0277	0.110	0.289	"
0.005	0.0112	0.158	0.280	Hudson
0.01	0.0121	0.121	0.230	"
0.03	0.0169	0.098	0.237	"
0.06	0.0253	0.103	0.258	"
0.10	0.0354	0.112	0.256	"

Summary.

1. Measurements of the rate of mutarotation of glucose at 24.°7 in acid (HCl) solutions between the strengths 0.001 and 0.1 molal have been made. They show that there is a linear relation between the hy-

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drogen ion concentration and the rate of mutarotation in solutions of such acid strength that the influence of the hydroxyl ions upon the rate can be neglected.

2. The conclusion of Osaka that the rate of mutarotation is proportional to the square root of the hydrogen ion concentration holds fairly well between the concentrations 0.01 to 0.10 molal but does not agree at all well with measurements outside this region of concentration.

3. Using Osaka's values for the rate in alkaline solution and new values for it in acid solutions, it is found that the following formula expresses accurately the rate of mutarotation of glucose at 25° in pure water and in acid and alkaline solutions. Rate $= 0.0096 + 0.258(H^{\cdot}) + 9750(OH')$.

4. Hydroxyl ions are nearly forty thousand times stronger catalyzing agents of the mutarotation of glucose than hydrogen ions.

5. This stronger catalyzing action of the hydroxyl ions causes a lower rate of mutarotation in weakly acid solutions than is observed for pure water. This depression of the rate, or "negative catalysis", has been measured in a 0.001 molal hydrochloric acid solution and found to be in close agreement with the predictions of the above formula.

The measurements recorded in this article were made possible by the kindness of Professor Geo. A. Hulett, who allowed the author the use of of his well equipped laboratory at Princeton University.

Newport News, Virginia.

COLLODION MEMBRANES.

BY S. LAWRENCE BIGELOW AND ADELAIDE GEMBERLING.

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Contents.

Bibliographical.—Comparison of dialysis through collodion, parchment paper and gold beater's skin.—The quantity of water which passes through collodion at a definite temperature and pressure.—Pressure and temperature coefficients.—The effect of thickness on the permeability.—The permeabilities of different samples of collodion.—The effect of age on the permeability. Summary.

The convenience and usefulness of collodion membranes are not, at the present time, fully appreciated by chemists and physicists. This article contains a brief bibliography, methods for making these membranes and an account of our experiments.

Bibliographical.

The first mention of collodion membranes as applied to diffusion phenomena, which we have found, is in an article by A. Fick[1]. He recognized their advantages but had difficulties in fastening them onto holders

[1] Ueber Diffusion. Pogg. Annal., 94, 59-86 (1855).

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and abandoned their use. W. Schumacher[1] had more success with them and devised a method for making small closed tubes or sacs of collodion with which he carried out a variety of experiments. But these were not numerous enough nor methodical enough to serve as the basis for any important conclusions regarding osmosis or the action of membranes.

An article by Baranetzky[2] contains more information about the chemical and physical properties of collodion membranes than any other which we have as yet found. He made collodion membranes, 5 cm. in diameter, in cells built up with filter paper on a glass plate. He observed, that, in order to make these membranes permeable to water, they must be put in water before the solvents have completely evaporated. The ether of the solvent evaporates quickly, and soon the membrane contains almost exclusively alcohol, this alcohol is replaced by water, and the resulting membrane is permeable to the latter. But if the membrane dries, it becomes hard and brittle, and when put in water absorbs only an insignificant quantity and remains impervious to that solvent. We have thus, with collodion, a method for obtaining membranes, otherwise alike, but differing in permeability. The way in which the gradual diminution in the size of the interstices in collodion may be stopped by plunging it into water, may be likened to the arresting of the development of a photographic plate by washing and dipping into a fixing bath. A collodion membrane, under water, retains for a good while the particular density or structure which it happens to have reached through evaporation of the solvents before immersion; after several weeks, however, it contracts somewhat.

Like Schumacher, Baranetzky worked exclusively with solutions and was particularly interested in showing that Jolly's "endosmotic equivalent"[3] was of no great significance, and in substantiating Brücke's theory[4] regarding the passage of substances through membranes. His results show that pyroxylin membranes are distinguished from others, such as animal membranes, parchment paper, and cellulose, by a less permeability for dissolved salts.

Neither Graham[5] nor Pfeffer[6] made use of collodion membranes; they have been overlooked or neglected by chemists and physicists since 1872. References to them are more numerous in medical literature. Interest-

[1] Ueber Membrandiffusion. Pogg. Annal., 110, 337-370 (1860).

[2] Diosmotische Untersuchungen. Pogg. Annal., 147, 195-245 (1872).

[3] Jolly. Ph. Experimental-Untersuchungen Ueber Endosmose. Pogg. Annal., 78, 261-271 (1849).

[4] E. Brücke. Beiträge zur Lehre von der Diffusion tropbarflüssiger Körper durch poröse Schneidewände. Pogg. Annal., 53, 77-94 (1843).

[5] On Osmotic Force. Phil. Trans., 144, 177-228 (1854). Liquid Diffusion applied to analysis. Phil. Trans., 151, 183-224 (1861).

[6] Osmotische Untersuchungen, Leipzig, 1877.

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ing applications of collodion sacs[1] and capsules in bacteriological investigations are described by Morpurgo and Tirelli[2], Metchnikoff, Roux and Salimbeni[3], Nocard and Roux[4], Vincent[5], Nocard[6], Novy[7], Gorsline[8], Crendiroupoulis and Ruffer[9], McCrae[10], Grubbs and Francis[11], Harris[12], Rodet and Guechoff[13], and Levy[14].

[1] The most convenient method yet devised for making collodion sacs large enough for carrying out separations by dialysis in the chemical laboratory is that of Novy. As these sacs are admirably adapted for lecture demonstrations and other purposes and as the references given may not be convenient, a description of the method follows:—A small orifice one or two mm. in diameter, is blown in the bottom of a tube of the diameter of the sac which it is desired to make. This hole is first closed with a layer or two of collodion, care being taken not to allow any collodion to go through the opening to the interior of the tube. This closing is conveniently accomplished by touching the bottom of the perforated tube with a cork carrying some collodion solution, allowing time for a portion of the solvent to evaporate, touching again, and so on until the closure is of the desired thickness. A flask, or cylinder, containing the collodion solution is tipped so that the tube mold, or "roll-tube", may be inserted and may be rotated just touching the surface of the collodion for a length somewhat in excess of that of the sac to be made. The tube thus coated with collodion, is taken out of the flask and a short time is allowed for some of the solvent to evaporate. It may then be inserted in the flask and rotated once more to give it another coat, and these operations may be repeated until the collodion membrane has acquired almost any desired thickness. But it is desirable to use a collodion of such consistency that one insertion and rotation suffices. When the coating has "set" and does not stick to the finger, the tube is plunged into water and water is poured into the interior. If the collodion is immersed in water too soon it becomes white and opaque, somewhat brittle and not durable. If the immersion is too long delayed, the collodion is apt to adhere to the tube so firmly that it is difficult to remove it without tearing. The proper interval, varying between two and 15 minutes, according to the consistency of the original collodion, is easily learned in two or three trials. By blowing into the tube and simultaneously pulling and twisting the membrane gently, the water is forced through the perforation and between the collodion membrane and the tube. With moderate care it is not at all difficult to detach the very transparent and tough collodion sac. There appears to be almost no limit to the size of the sacs which may thus be made. Novy and Gorsline's sacs for their striking demonstrations of the phenomena of dialysis were frequently 40 cm. long by 2-3 cm. in diameter.

Dialysis occurs with great rapidity through such sacs and the whole process can be watched without the least difficulty because of their transparence.

[2] Arch. ital. biol., 18, 187-192 (1893).
[3] Ann. inst. Pasteur, 10, 261 (1896).
[4] Ibid., 12, 240 (1898).
[5] Ibid., 12, 787 (1898).
[6] Ibid., 12, 564 (1898).
[7] Laboratory work for Bacteriology by F. G. Novy, 1899, 499.
[8] C. S. Gorsline "On the Preparation and Use of Collodion Sacs," "Contributions to Medical Research" dedicated to Dr. V. C. Vaughan, 1903, 390-394.
[9] Compt. rend. soc. Biol., 52, 1109-1110 (1900).
[10] J. Exp. Med., 6, 635 (1901).
[11] Bulletin No. 7 of the Hygienic Laboratory of the U. S. Marine Hospital Service, 1902.
[12] Muir and Ritchie's Manual of Bacteriology, American edition, 1903, 67.
[13] Compt. rend. soc. Biol., 52, 965-67 (1900).
[14] J. Infectious Diseases, 2, 1-48 (1905).

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Gorsline found that pepton, albumose, starch, dextrin, albumin and enzymes, employed in from one-half to one per cent. solutions all passed through his collodion sacs in less than twenty-four hours at a temperature of 35° in sufficient quantities to give positive tests. Because they permit the passage of colloidal substances in small quantities, it should not be inferred that these membranes are inferior to others for the purpose of dialysis. The process of dialysis does not furnish us with positive means of separation, but just as we may accomplish much by fractional distillation and crystallization, so may we by fractional dialysis. Graham recognized this clearly enough and recorded the facts that albumin, starch, etc., passed through his parchment paper and animal mucous membranes, though in much smaller quantities, relatively, than crystalloids. That the permeability of a membrane for different substances is relative, that there is no such thing known as a strictly semi-permeable membrane, but only membranes through which one substance passes much more slowly than do other substances, has always been understood and recognized. That one substance passes in and another out, and that what we observe in every case is the resultant of oppositely directed streams, is not a discovery of the last few years. This is clear enough from the old terms, endosmosis for the passage inward, and exosmosis for the passage outward, terms first suggested and defined by Dutrochet[1] in 1827.

Malfitano[2] filtered a solution containing a colloid to which he ascribed the formula $HN(Fe_2O_6H_6)Cl$ through collodion and found that the greater part of the colloid was held back by the filter. Bierry and Giaja[3] made the interesting observation that pancreatic secretion having passed through a collodion membrane, no longer acted on starch or maltose, but that adding an electrolyte, preferably one containing a chlorine or bromine ion to this inactive material restored its lost activity and ability to act on starch.

This bibliography might be extended, and such extension would probably not be without interest to chemists. But enough has been given to show that collodion membranes in one form or another are frequently employed by bacteriologists, seldom by chemists and physicists, and that they are attractive and promising objects of study.

Experiments.

Dialysis Through Collodion, Parchment Paper and Gold Beater' Skin.—We wished to ascertain, by direct experimental comparison, the relative efficiencies of collodion, parchment paper and gold beater's skin, for separations by dialysis as ordinarily carried out in the laboratory. A collodion solution was made according to the directions in the U. S.

[1] Dutrochet. Nouvelles observations sur l'Endosmose et l'Exosmose, et sur la cause de ce double phénomène. Ann. chim. phys., 35, 393-400, (1827).

[2] Compt. rend., 141, 660-62, (1905).

[3] Compt. rend. soc. biol., 62, 432, (1907).

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Pharmacopoeia. Seventy-five cc. of ethyl ether were poured over 3 g. of commercial pyroxylin[1] in a flask with a cork to prevent the rapid evaporation of the solvent. After ten or fifteen minutes 25 cc. of ethyl alcohol were added and the pyroxylin dissolved quickly and completely to a clear, rather mobile, liquid requiring no filtration. The preliminary soaking in ether materially hastens the solvent action. Other proportions of solvents and solute may be used. A few cc. of this collodion solution were poured upon a clean dry piece of plate glass and were spread by tilting the glass to and fro, over an area about half again as large as the membrane we wished to make. This layer was allowed to dry until it was of a gelatinous consistency and did not wrinkle when the finger was rubbed lightly across it. Its edges were then loosened and it was peeled off. The largest membrane we made was perhaps 20 cm. in diameter, but larger ones could have been made if they had been wanted. The membranes were fairly uniform in thickness, between 0.2 and 0.4 mm. as measured by a micrometer caliper. After the work described in this article had been completed, one of us found that membranes of great uniformity of thickness could be made by pouring the collodion onto a surface of mercury in a shallow dish.

Three dialysers of the common type and of nearly the same size (9 cm. in diameter) were selected. A collodion membrane was made and placed immediately on a dialyser, the surface that had been next the plate being next the rim. It was stretched tightly, and drawn up over the rounded sides to which it conformed without wrinkles, owing to its plasticity. A coating of collodion painted on the joint made this secure, and tying with string was not necessary. While the membrane was being attached to the dialyser, its surface was kept moist by laying upon it a piece of moist filter paper.

Gold beater's skin, such as is sold in strips by surgical supply houses. was tied on the second dialyser with numerous turns of strong thread. Parchment paper was attached in the same manner to the third dialyser.

One hundred cc. of a solution of red colloidal gold, made according to the directions given by Zsigmondy[2] were put in each of the dialysers, and all three were suspended in one large low ice jar of distilled water. The rate of dialysis was followed by determining the conductivities of the solutions by means of a Kohlrausch "Tauchelektrode" every twenty-four hours. The water in the jar was changed each day, immediately after the determinations of the conductivities. When the conductivity of the solutions had fallen to nearly that of ordinary distilled water, this was replaced by water showing a conductivity of 1.2×10^{-6}. The results

[1] Detailed and interesting information regarding pyroxylin is given in a recent article by G. Lunge. "Zur Kenntniss der Kollodionwolle". Z. angew. Chem., **19**, 2051-58, (1906).

[2] Z. anal. Chem., **40**, 697-719, (1901).

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obtained are given in Table 1. All the values for the conductivities should be multiplied by the common factor 10^{-6}.

TABLE 1.

Time of dialysis in days	Gold-beater's skin. Conductivity.	Collodion. Conductivity	Parchment paper Conductivity
0	984.2	984.2	984.2
1	304.7	415.6	850.0
2	81.3	207.8	467.5
4	55.3	102.4	255.8
5	29.9	85.0	158.5
10	22.7	26.3	47.1
11	16.7	(30.4)	(50.5)
12	*11.0*	21.0	43.1
13	10.1	17.3	27.1
14	7.9	14.0	17.3
17	8.1	*11.0*	14.9
18	8.0	12.4	13.9
19	...	11.0	*11.0*

Some intermediate values obtained are omitted from the table. We have no explanation to offer for the high values to which we call attention by enclosing them in brackets.

If we consider the time required for dialysis to proceed to the same point, say until the conductivity has been diminished to 11×10^{-6} we see that this is accomplished by the gold beater's skin first, in 12, by the collodion second, in 17, and by the parchment paper last, in 19 days. If we compare the conductivities of the solutions in the three dialyzers on the fourth day we find the conductivity in the parchment to be about twice what it is in the collodion, and in the collodion about twice what it is in the gold beater's skin. Approximately this relationship is maintained for eight days.

We carried out similar experiments with $Fe(OH)_3$ and $Al(OH)_3$ as the colloids. The volumes of liquid in the dialyzers with the gold beater's skin and with collodion membranes increased rapidly owing to osmosis, and these dialyzers repeatedly overflowed. It is worth noting that the dialyzers with parchment membranes did not do this. The following is an example of the results we obtained: In 20 days the conductivity of a solution containing colloidal ferric hydroxide fell off 287×10^{-6} in the gold beater's skin dialyzer, 265×10^{-6} in the collodion dialyzer, and only 55×10^{-6} in the parchment dialyzer.

These comparisons measure the relative merits of the three membranes for effecting separations by dialysis. Gold beater's skin is the best membrane, collodion is next and parchment paper, which is undoubtedly the most generally used, is the least good.

A. Zott[1] carried out an extensive investigation, comparing dialysis

[1] Ueber die relative Permeabilität verschiedener Diaphragmen und deren Verwendbarkeit als dialytische Scheidewände. Wied. Annal., 27, 229-289, (1886).

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through fifteen different membranes. Collodion was not included among them. He says that only three are useful in practise, namely, gold beater's skin, pig's bladder and parchment paper, and, of these three, gold beater's skin is distinctly the best, while parchment paper is the poorest.

We tried to strengthen collodion membranes by making them with cotton net inside and so enlarge their field of usefulness. The net was easily incorporated in the collodion by laying it on the plate glass and pouring the solution on it. We found, however, that the meshes of the fabric were not readily covered, and that we could not be sure that we had perfect membranes without leaks. Our membranes, as we were making them, appeared strong enough for all ordinary purposes, indeed collodion membranes are tougher than one not familiar with them would suppose, and so we did not pursue this work further. If a membrane requires reinforcement, this can be given by letting the membrane and dialyzer rest on wire gauze, as is frequently done in experiments upon osmosis.

The Effect of Changes in Temperature and Pressure on the Permeability of Collodion Membranes.

Apparatus and Method of Measurement.—We made some quantitative determinations upon the rate at which water passes through collodion membranes, at a definite temperature and pressure, and also upon the effects of changes of pressure and of temperature on this rate. Very little bearing upon these questions is to found in the literature. Schmidt[1], who studied the rate at which water and various solutions pass through animal membranes, did not work with collodion, and Schumacher[2] and Baranetzky[2] confined their attention to determining the quantities of dissolved salts which passed through their membranes.[3]

The arrangement of the apparatus is shown in Figure 1.

A,A,A, are the membrane holders. C,C,C, are pinch cocks by means of which any one holder can be cut out. D is a safety bottle. E is a mercury manometer measuring the diminished pressure in the apparatus. F is a stone jug of about 20 liters capacity. G is a tube provided with a stop cock leading to a water aspirator. H is an Ostwald thermostat of the usual type with the usual temperature regulation and system of stirring. I is a glass jar immersed in the thermostat and containing distilled water into which the membrane holders dip.

The membrane holders were made by sealing pieces of common glass tubing, about 2.5 cm. long, the smallest having an internal diameter of

[1] W. Schmidt. Versuche über Filtrationsgeschwindigkeit verschiedener Flüssigkeiten durch thierische Membran. Pogg. Ann., 99, 337-88 (1856).

[2] Loc. cit.

[3] This literature will be considered more fully in an article by one of us to appear in the next number of this journal.

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11.67 mm., the largest an internal diameter of 11.89 mm., onto capillary tubing. The capillary tubes were 28 cm. long and of such internal diameter that approximately two cc. were contained in a length of 21 cm. Thus one mm. length contained about 0.0097 cc. It was easy to read the height of a water column within these tubes to less than ½ mm.; therefore our measurements of volume were within 0.005 cc. of right.

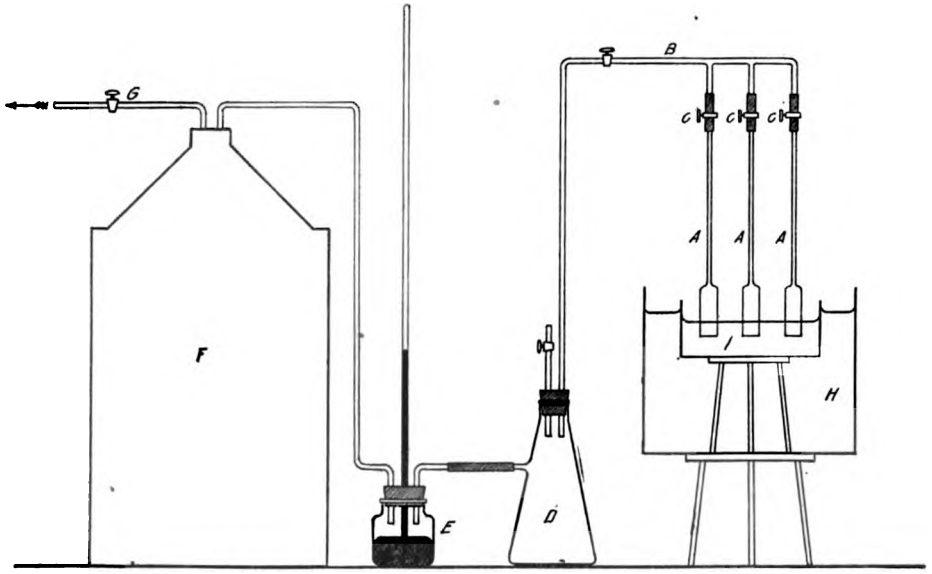


FIGURE 1.

We etched scales on these tubes and then calibrated them for intervals of 0.2 cc. by weighing them out with mercury. The membranes, made as already described, were fastened on in the same manner in which we fastened them onto other dialyzers, only we found it desirable to wind the joint with thread besides painting it with collodion.

The method of carrying out an experiment is evident from the figure. The tubes were filled with water nearly up to the lowest mark on the scale, and were then attached to the arm B. Suction was applied until the manometer showed the desired diminution of pressure within the apparatus. The difference between the barometric height and the height of the mercury in the manometer, we have called the "driving pressure" in the tables. A few moments were allowed for the flow of water through the membranes to become regular before the initial readings were taken. Readings were made at the expiration of five or fifteen minute intervals, measured by means of a stop watch. The volume of the jug being large, the very small diminution in volume caused by the entrance

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of water into the experimental tubes was quite negligible. The pressure within the apparatus frequently remained practically unchanged for twenty-four hours. During no experiment, which was accepted as of value, did the pressure fall off as much as five mm.

Varying the pressure, temperature being held constant.—The results of a typical series of experiments with three membranes are contained in Table 2. Reading were made at intervals of five minutes and were corrected by the calibrations of the tubes.

TABLE 2.

TEMPERATURE 25° ± 0°.2. DRIVING PRESSURE 150 MM. ± 2.5 MM.

Tube I		Tube II		Tube III	
Readings	Diff. or volume in cc.	Readings	Diff. or volume in cc.	Readings	Diff. or volume in cc.
1.500		1.685		1.790	
	0.085		0.075		0.075
1.415		1.610		1.715	
	0.065		0.065		0.040
1.350		1.545		1.675	
	0.080		0.095		0.045
1.270		1.450		1.630	
	[0.030]		[0.120]		[0.090]
1.240		1.330		1.540	
	[0.190]		0.065		0.065
1.050		1.265		1.475	
	0.080		0.080		0.040
0.970		1.185		1.435	
	0.075		0.055		0.030
0.895		1.130		1.405	
	0.075		0.055		0.040
0.820		1.075		1.365	
Mean values	0.084 cc.		0.076 cc.		0.056 cc.

The bracketed values show wide divergence from the rest. We call attention to them as being the largest fluctuations, without obvious cause, which we observed in our numerous measurements.

The series was repeated 11 times giving us 11 tables similar to Table 2. The results may be summed up as follows :—The average of 78 separate readings for tube I showed that 0.074 cc. of water passed through the membrane in five minutes. The average of 80 readings for tube II showed that 0.068 cc. of water passed through its membrane in five minutes, and the average of 77 readings for tube III showed that 0.044 cc. of water passed through its membrane in five minutes.

Experiments similar to those of Table 2 were performed with the same membranes for pressures of 50 and 250 mm. Table 3 contains the results of one of 16 series with a pressure of 50 mm. Table 4 contains the results of one of 11 series with a pressure of 250 mm. The values are cc. of water passing through in five minutes.

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TABLE 3.

TEMPERATURE 25° ± 0.°5. DRIVING PRESSURE 50 MM. ± 2.5 MM.

Tube I	Tube II	Tube III
0.030	0.030	0.020
0.020	0.020	0.010
0.040	0.040	0.030
0.025	0.020	0.020
0.030	0.020	0.010
0.030	0.025	0.015
0.020	0.015	0.010
0.015	0.030	0.015
....	0.025	0.015
Mean values, 0.026	0.025	0.016

TABLE 4.

TEMPERATURE 25.° ± 0.°5. DRIVING PRESSURE 250 MM. ± 2.5 MM.

Tube I	Tube II	Tube III
0.095	0.110	0.045
0.085	0.070	0.055
0.095	0.085	0.050
0.090	0.075	0.055
0.090	0.095	0.050
0.100	0.090	0.065
0.085	0.090	0.065
....		0.045
....		0.060
Mean values, 0.091	0.087	0.054

Table 5 contains the means of all the values obtained at the three pressures.

TABLE 5.

	50 mm.		150 mm.		250 mm.	
	Number of observations	cc. of water in 5 mins.	Number of observations	cc. of water in 5 mins.	Number of observations	cc. of water in 5 mins.
Tube I....	98	0.030	78	0.074	70	0.120
Tube II...	99	0.028	80	0.068	77	0.108
Tube III..	96	0.017	77	0.044	81	0.076

We are unable to say why the membrane on tube III showed a lower permeability than those on tubes I and II.

We divided the increase in volume of water passing per unit time by the corresponding increase in pressure, and calculated what percentage this was of the volume passing when the pressure was 150 mm. This gave us what might be called a pressure coefficient of the permeability. The results of these calculations are given in Table 6.

TABLE 6.

Tube I				Tube II			Tube III		
Pressure	Obs. volume	Diff.	Press. coeff.	Obs. volume	Diff.	Press. Coeff.	Obs. volume	Diff.	Press. coeff.
50	0.030			0.028			0.017		
		0.044	0.59%		0.040	0.59%		0.027	0.61%
150	0.074			0.068			0.044		
		0.046	0.62%		0.040	0.59%		0.032	0.66%
250	0.120			0.108			0.076		
Mean values			0.60%			0.59%			0.63%

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Temperature being held constant at 25°, a change of 1 mm. in the pressure causes a change in the rate at which water passes amounting to about 0.6 per cent. of the volume of water which passes when the driving pressure is 150 mm.

It is interesting that in spite of the divergence between the actual experimental values for different membranes, all the pressure coefficients are nearly the same.

The permeability of the membranes at constant temperature, appears to us to be very nearly, but not quite, a linear function of the driving pressure. This same conclusion was reached by Schmidt[1] for his animal membranes from less experimental evidence.

Varying the Temperature, Pressure Being Held Constant.—We used the same three membranes as before, the uniform driving pressure of 150 mm. mercury, and determined the volumes of water which passed through during fifteen minute intervals. We made six separate observations for each of the three tubes at 5°, and at 45°, and 18 separate observations for each of the three tubes at 15°, 25° and 35°. Table 7 contains a summary of the results. The volumes given are the means of all observations at each temperature.

TABLE 7.

	Tube I		Tube II		Tube III	
Temp.	cc. passing in 15 mins.	Diff.	cc. passing in 15 mins.	Diff.	cc. passing in 15 mins.	Diff.
5°	0.086		0.080		0.063	
		0.021		0.020		0.025
15°	0.107		0.100		0.088	
		0.043		0.033		0.022
25°	0.150		0.133		0.110	
		0.023		0.030		0.032
35°	0.173		0.163		0.142	
		0.034		0.062		0.036
45°	0.207		0.225		0.178	

The results are so irregular that we do not feel justified in calculating a temperature coefficient to correspond to our pressure coefficient. However, we think they show that such temperature coefficient is not a linear function, but increases slightly with the temperature. It will be observed also that the amount of water passing per unit time is about doubled when the temperature is increased 20° to 30°.

Varying the Thickness of the Membranes.—Attempts were made to determine the thickness of the membranes and its influence on the permeability. Of course the membranes are thicker when full of water and thinner when dried out. We secured six membranes of different thicknesses, by varying the amount of tilting to and fro of the glass plate on which they were made. We fixed these on six tubes and measured the amount of water which passed through in one hour at a temperature of 25°. We then removed the membranes from their tubes, pressed them lightly be-

[1] Loc. cit.

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tween filter paper, and measured the thickness with a micrometer caliper at ten different points on each membrane. We allowed the membranes to dry for several days in a desiccator and weighed them, merely as a check on our micrometer measurements. The diameter of the largest membrane was 11.89 mm., of the smallest 11.67 mm. Table 8 contains the results. Only the means of each ten readings of the caliper are included.

TABLE 8.

Temperature 25°.

	1	2	3	4	5	6
Thickness in mm.....	0.31	0.20	0.13	0.34	0.33	0.42
Cc. of water in one hour...	0.45	2.04	1.25	0.83	0.86	1.05
Weight in mg. when dry...	4.4	3.0	2.0	4.4	3.9	5.4

These values are not regular enough to establish any mathematical relations. They show that while the permeability undoubtedly falls off as the thickness increases, as is to be expected, other influences also are at work which have an even greater effect on the permeability than the thickness.

As already noted, Baranetzky[1] stated that if one membrane be allowed to dry out more than another before it is immersed in water it will be less permeable. We tested this experimentally, taking one membrane off the glass plate as soon as its consistency would permit, and leaving another on as long as we could. We found that the interval of varying moisture between which useful membranes can be taken off is rather narrow. They obviously cannot be taken off too soon, but on the other hand, if they dry out too much they are apt to stick to the plate and tear. The time interval however, is not inconveniently short, because the upper surface dries quickly, and this retards evaporation from the interior. Our numerical results are too irregular to serve as proof, but our experience leads us to believe that while the different degrees to which the membranes may have dried out, as we made them, affected their permeabilities to a certain extent, this alone is not sufficient to account for the irregularities in Table 8.

Different Collodions.—We observed marked differences in the permeabilities of membranes made from different samples of pyroxylin. In Table 9, tubes I, II and III carried membranes of collodion made from pyroxylin kindly furnished us by the School of Pharmacy of the University of Michigan. Tubes IV, V and VI carried membranes of collodion

TABLE 9.

Driving Pressure	I	II	III	IV	V	VI
50 mm.	0.078	0.075	0.048	0.018	0.018	0.008
	0.080	0.075	0.047	0.015	0.015	0.013
150 mm.	0.225	0.220	0.143	0.047	0.048	0.023
	0.207	0.185	0.122	0.043	0.040	0.020
250 mm.	0.357	0.345	0.190	0.067	0.073	0.032
	0.367	0.323	0.240	0.067	0.063	0.032

[1] Loc cit.

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made from commercial pyroxylin. The values are cc. of water passing in 15 minutes at a temperature of 25°, each value given being the mean of three separate measurements.

In spite of the differences in the values obtained with different collodions, what we have called the pressure coefficient remains practically the same. Calculating the same way as before, we find a pressure coefficient for the membrane on tube IV of 0.57 per cent., for the membrane on tube V of 0.60 per cent., and for that on tube VI of 0.55 per cent.

The membranes made from the commercial collodion were less durable than the others. They frequently broke under low pressures before the third day, though some lasted as long as fifty days. Their average "life" was 20 days as compared to 50 or 60 days for membranes made from our other pyroxylin.[1]

Effect of Age on the Permeability.

The membranes become less permeable as they grow older. Table 10 contains results demonstrating this. The values given are cc. of water passing in five minutes, and all the values in this table were obtained with one membrane. The age of the membrane is given in days.

TABLE 10.

TEMPERATURE 25° ± 0.°5.

Driving pressure	50 mm.	150 mm.	250 mm.
Age 3 days	0.032 cc.		
	0.032		
4 days	0.027		
	0.043		
	0.024		
13 days	0.054	0.082 cc.	0.129 cc.
	0.034	0.086	
14 days	0.028	0.080	0.112
15 days	0.022	0.066	0.098
20 days	0.031	0.076	0.112
	0.024	0.074	0.107
21 days	0.028	0.062	0.106
	0.022	0.060	0.106
22 days	0.021	0.055	0.104
25 days	0.018	0.055	0.102
	0.017	0.043	0.099
		0.060	0.080
	0.021	0.056	0.085
29 days	0.017	0.047	0.073

[1] We were unable to obtain details regarding the particular method of preparation of the commercial pyroxylin, there being, apparently, some trade secret involved, and we are, therefore, not in a position to offer an explanation of the difference in permeabilities. Judging from the information contained in Lunge's article (loc. cit.) we are inclined to believe that the commercial pyroxylin was made by nitrating cotton for a longer time, or at a higher temperature, than that employed in the School of Pharmacy. We intend at some future time to make pyroxylin by different methods and compare the permeabilities of the resulting membranes.

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In spite of some wide variations, for which we are unable to account, it is evident from this table that the permeability diminishes as the age increases. At the end of four weeks the membrane showed about half its original permeability.

Summary of Results.

1. Collodion membranes in the form of sacs, or flat films, for ordinary dialyzers, even of large size, are easily made. They may be attached to supports more neatly and more perfectly than parchment paper. Dialysis occurs through them more rapidly, and therefore they are to be preferred to the more commonly used material. Membranes of gold beater's skin, however, are still better for separations by dialysis.

2. The quantity of water passing through collodion membranes is nearly a linear function of the pressure, the temperature being held constant.

3. An attempt to calculate a "pressure coefficient" of permeability for 25° gave the result :—A change of 1 mm. in pressure causes a change in the volume of water passing equal to about 0.6 per cent. of the quantity which passes when the pressure is 150. mm. mercury.

4. The quantity of water passing, pressure being constant at 150 mm. is not a linear function of the temperature. A "temperature coefficient" was not established but an increase of 20° to 30° was required to about double the quantity of water passing per unit time.

5. Different samples of collodion showed different permeabilities, but in spite of the differences in the absolute values, a change of pressure or of temperature produced the same proportional effect in all.

6. As a collodion membrane grows older, its permeability diminishes gradually, but it lasts and remains useful for one to three months.

UNIVERSITY OF MICHIGAN.
August, 1907.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 146].

THE DETERMINATION OF CARBON MONOXIDE IN ATMOSPHERIC AIR.

BY J. LIVINGSTON R. MORGAN AND JOHN E. MCWHORTER.
Received September 14, 1907.

All the satisfactory methods for the quantitative estimation of small amounts of carbon monoxide are based upon the reaction,

$$I_2O_5 + 5CO = 5CO_2 + I_2,$$

which was first observed by Ditte,[1] and which, according to Kinnicutt and Sanford,[2] is only quantitative at 150° or above, although Gautier[3] re-

[1] Bull. soc. chim., 13, 318 (1870).
[2] This Journal, 22, 14 (1900).
[3] Compt. rend., 128, 487 (1899).

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gards it as complete at 60°–70°. In all the methods based upon this reaction, and there are practically no others, the air to be analyzed is first passed through U-tubes containing potassium hydroxide and sulphuric acid (which remove all the other gases reacting with the iodine pentoxide as carbon monoxide does), and then through a U-tube containing iodine pentoxide, heated in an oil or glycerol bath to the proper temperature. It is only in the subsequent treatment of the products (iodine and carbon dioxide) produced by the reaction, carried out in this way, that the various methods differ from one another. Gautier[1] removed the iodine by passing the gas issuing from the iodine pentoxide tube over heated copper, collected the carbon dioxide by absorption in caustic soda solution, and then later liberated it with sulphuric acid and measured its volume in a graduated tube which had been exhausted by a Sprengel pump; a method which would hardly recommend itself to the practical chemist. Nicloux[2] determined the amount of iodine set free by the depth of color in chloroform solution. And finally Kinnicutt and Sanford[3] absorbed the iodine in a potassium iodide solution, titrating it subsequently with N/1000 sodium thiosulphate; but were not able to obtain accurate determinations by either of the other methods. Tóth[4] has also used this method for the estimation of carbon monoxide in tobacco smoke, with very good results, although the iodine pentoxide was heated to only 60°–70°.

In analyzing the compressed air in the East River Pennsylvania tunnels for the constructors, Messrs. S. Pearson & Son, Inc., we have had occasion to study the various methods for the determination of carbon monoxide, and, after considerable initial difficulty, have succeeded very well with that of Kinnicutt and Sanford. The difficulty we experienced was the continuous, apparently spontaneous, decomposition of the iodine pentoxide, even below 100°, when enclosed in a glass-stoppered U-tube, with lanoline as the lubricant. The cause of this decomposition, which was observed with all specimens used, was finally found to be the traces of lanoline which were drawn into the tube by the suction, together with the hot glycerol of the bath, with which the cool portions of the tube were bathed in order to drive out the last portions of the iodine. The remedy for this, of course, is to seal off the ends of the iodine pentoxide U-tube, in a blast lamp after filling, for experiment shows that all animal fats at 150° or less react violently, even explosively, with iodine pentoxide. It is strange that this precaution is not mentioned in any of the above papers, for it is natural for one to select a glass-stoppered tube, since rubber and cork are

[1] Loc. cit.
[2] Compt. rend., 126, 746 (1898).
[3] Loc.cit.
[4] Chem.-Ztg., 98, (1907).

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out of the question, and the slightest trace of the lubricant in the tube will cause high results to be obtained.

Although by this method our results (all at 150°, for the sake of rapidity) were very satisfactory, we finally resorted to a modification of it which has many advantages, for it is somewhat simpler, and, with very little trouble, enables one to get checks by two methods on the same sample of gas, thus eliminating the possibility of error. The modification is exceedingly simple. It consists in passing the iodine free gas issuing from the potassium iodide tube, used by Kinnicutt and Sanford, through a long test tube (24. × 2.5 cm.) containing 50 cc. of the solution of barium hydroxide used for the determination of carbon dioxide in air by Hesse's method, and finding the volume of carbon dioxide absorbed by titration with the standard solution of oxalic acid usually used for this purpose, *i. e.*, one containing 1.12650 g. of crystallized oxalic acid in one liter of water, using phenolphthalein as indicator. Tests on measured and unmeasured amounts of pure carbon monoxide mixed with air (See table below) show that by titrating both the iodine absorbed in the potassium iodide, and the carbon dioxide in the barium hydroxide solution, very satisfactorily checking results are obtained, showing that it was only the difficulty in measuring the volume of carbon dioxide by Gautier's method, and not the principle upon which the method is based, that prevented Kinnicutt and Sanford from obtaining accurate results for carbon monoxide by the determination of the carbon dioxide set free.

Every cubic centimeter of carbon monoxide, measured at 0° and atmosmospheric pressure, liberates 0.00227 g. of iodine, and 1 cc. of carbon dioxide, *i. e.*, enough to transform into carbonate, the amount of the barium hydroxide solution which is equivalent to 5 cc. of the above oxalic acid solution.

One advantage of this modified method is observed when it is necessary to determine the amount of carbon dioxide, as well as of carbon monoxide, in the air. Then it is simply necessary to place another narrow test tube, containing 50 cc. of the barium hydroxide solution, in front of the caustic potash and sulphuric acid tubes. In this way, by the same reagents, the amount of free carbon dioxide is found by titration of the contents of the first barium hydroxide tube, and the amount of free carbon monoxide, transformed into dioxide by titration of the contents of the second; and all in one operation.

COMPARISON OF METHODS FOR CO.

	Per cent. CO Found.	
Per cent. CO taken.	Iodine titration.	CO_2 titration.
0.0803	0.081	0.0850
0.0838	0.0859	0.0820
Unknown	0.0454	0.0480
"	0.0465	0.0460
"	0.0618	0.0613

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The results of this paper may be summarized as follows:

I. In the determination of carbon monoxide by passing it over heated iodine pentoxide, the ends of the U-tube should be sealed off after filling, since the presence of organic matter, such as might come from the lubricant used with glass stoppers, also causes the decomposition of the iodine pentoxide, and would give too high results.

II. A modified method for carbon monoxide is presented, in which, after the iodine formed by the reaction is removed by a potassium iodide solution, the carbon dioxide is absorbed in barium hydroxide solution and determined by titration with oxalic acid. A check on the same sample can then be obtained, if desired, by titrating the iodine absorbed in the potassium iodide solution with N/1000 sodium thiosulphate.

III. By placing another barium hydroxide tube before the one containing the iodine pentoxide, both the free carbon dioxide and the carbon dioxide produced by the free carbon monoxide, can be determined in one operation by two titrations with the same reagent.

LABORATORY OF PHYSICAL CHEMISTRY,
September, 1907.

RAPID ANALYSIS BY ELECTROLYSIS WITHOUT ROTATING ELECTRODES.

FRANCIS C. FRARY.
Received August 24, 1907.

In a preliminary paper[1] I have described two forms of apparatus for the rapid determination of metals in the electrolytic way, without the use of a motor or rotating electrodes. The purpose of this paper[2] is the description of the improved forms of this apparatus[3] as they have been worked out since the earlier publication.

In the first apparatus (fig. 1.) the solenoid consists of about 500 turns of 1.5 mm. insulated copper wire (about No. 14 B and S gauge) and is wound on a copper cylinder 6 cm. in diameter and 11 cm. high. The flanges on the end of the cylinder are of sheet-iron. A hollow iron cylinder (height 4 cm., thickness of iron 1 cm.) stands in the lower part of the copper cylinder. The solenoid is surrounded by an iron mantle, 2 mm. thick, which serves the double purpose of protecting the insulation of the solenoid and of presenting a short path for the magnetic circuit on the outside of the coil. In this way the entire magnetic force of the solenoid is concentrated in that portion of its core lying above the inner iron cylinder.

[1] Z. Elektrochem., 13, 308.

[2] Also published in the Z. angew. Chem.

[3] D. R. G. M. applied for by the Vereinigten Fabriken für Laboratoriumsbedarf, Berlin (American agents—The Kny-Scheerer Co., New York) who are sole owners of the right to manufacture the apparatus for sale, and to whom I am indebted for the | he two drawings here published.

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With this apparatus a cylinder of platinum foil, or of platinum, copper, silver or nickel gauze, is used as cathode. The gauze cathode is preferable and should be large enough to fit the beaker quite closely. The beaker, which should hold about 125-150 cc., is supported by the iron cylinder in the core of the coil. I have used a spiral anode of the form shown in the cut, with good results. If it were desired to use this apparatus for the separation of the metals under graded cathode-potential as recommended by Sand[1], the spiral could be made broader in order to

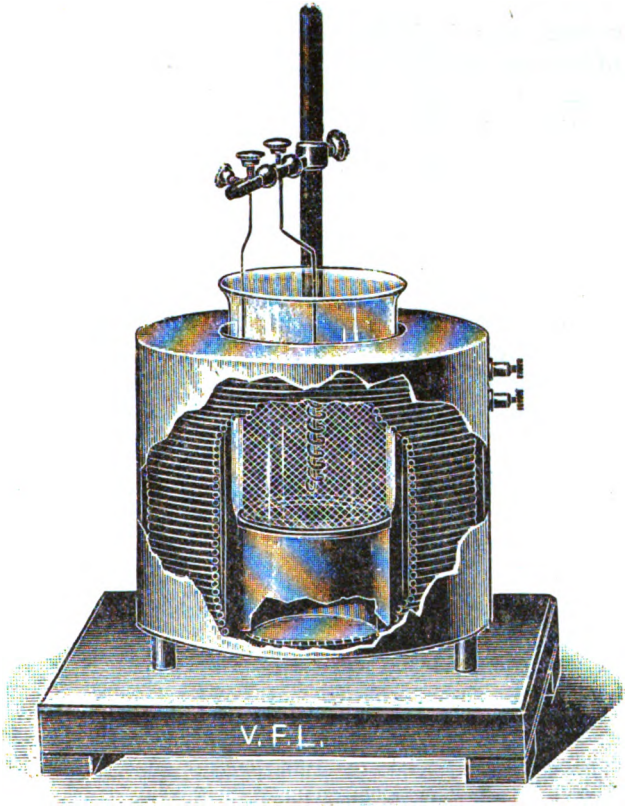


FIGURE 1.

secure the necessary low resistance of the bath. The electrolyte should, in general, just cover the cathode.

The electrolytic cell and the solenoid are generally connected in series so that only one source of current is required. The resistance of the coil is about one ohm, and five amperes may be sent through it for a long time without danger of overheating. As many electro-analytical methods require that the solution be heated, the heat developed in the coil is often

[1] J. Chem. Soc., 91, 373.

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no disadvantage. In cases where this heat is not desired, a smaller beaker (125 cc.) is used. This is surrounded by a spiral of lead pipe (4 mm.) through which water flows. If it is desired to use a small current for the electrolysis, the solenoid may be excited wholly or in part by a separate circuit.

For currents of more than 6 amperes the same method may be used, or a shunt may be used in parallel with the coil. If several pieces of the apparatus are in continual use in the same laboratory, all the coils may be connected in series and excited by the same current. The current-strength for each analysis is then regulated independently of all the others and of that through the coils.

When the current flows through the solenoid, a uniform magnetic field is produced in the beaker, the lines of force being vertical. If, now, the current passes from one electrode to the other through the electrolyte, the lines of current in the latter are radial and horizontal. Every infinitesimal strip of electrolyte between the electrodes acts as if it were a wire carrying a current. The current direction is in every case perpendicular to the magnetic lines of force, which, therefore, push the electrolyte in a direction perpendicular to their direction and to that of the current. In other words, every particle of the electrolyte between the electrodes is acted on by a horizontal force which pushes it in a direction perpendicular to a radius of the cylinder drawn through it. The whole electrolyte therefore revolves about the anode as a cylinder about its axis. The cathode is naturally the limit of the current lines, yet the portion of the electrolyte between it and the walls of the beaker revolves also, although much more slowly.

The same principle is used in the second apparatus (fig. 2) but the relative directions of the field and current are reversed. This apparatus is designed for use with a mercury cathode, the current lines are vertical, and a magnetic field of radial direction is therefore necessary. The cathode cell has been made larger than that generally recommended,[1] in order that a volume of 100-125 cc. of electrolyte may be used as conveniently as the volume of 10-20 cc. usually recommended. Richards and Bisbee[2] have shown that precipitation is much more rapid from a small volume of solution, nevertheless the time lost in the evaporation of the larger volumes of liquid usually obtained in analytical work, would often be more than that gained by the more rapid precipitation from the smaller volume.

In order to obtain the radial magnetic field necessary for the rotation, the cathode-cell is made so that it has, in cross section, the form of a ring,

[1] i. e. by Smith and Kollock: This Journal, 27, 1255, and Price and Judge, Chem. News, 94, 18 (1906).

[2] This Journal, 26, 530.

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as shown in the cut, and one pole of the magnet extends up into the inner tube. The other pole is brought up around the solenoid so that it takes the form of a ring surrounding the cell. The lines of force have thus an iron path through the whole magnetic circuit except where the cell stands, and practically the whole magnetic force of the solenoid is

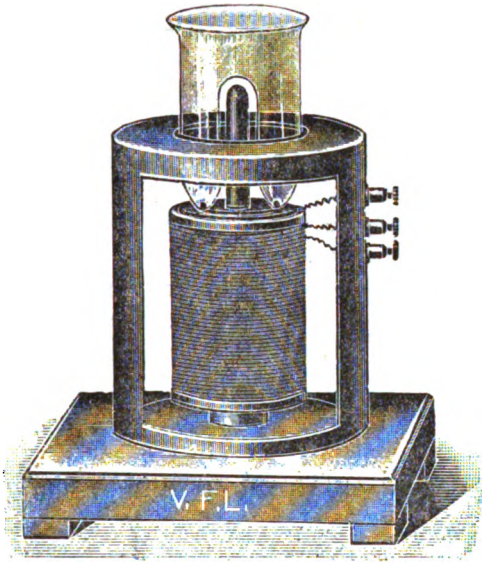


FIGURE 2.

concentrated in this gap, just where it is desired. The very strong "stray field" of the earlier model is thus avoided. The diameter of the cathode cell is 5 cm. and its height 10 cm. It has a capacity of 200 cc. and thus gives room for the rather strong boiling and frothing which sometimes takes place. It is made of Jena glass, and rests upon three platinum wires fused into the glass and projecting into the mercury inside. The coil has 500 turns of 1.1 mm. insulated copper wire (No. 16 B and S gauge) and is wound on an iron core 1.6 cm. in diameter. On the upper end of the coil is fastened an insulated copper plate, which is connected with the negative pole of the source of current, and makes contact with the mercury cathode through the above-mentioned platinum wires.

In order to measure the rate of stirring of the liquid in this cell, a fragment of filter-paper was thrown into it and a current of 3.4 amperes sent through the cell and coil (connected in series). Both the path and speed of the paper were irregular; at times it would sink to the surface of the mercury and then again it would rub on the anode. I counted the number of revolutions per minute and found in three trials the numbers 100, 102 and 104. With the use of larger currents I was unable to measure

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the rate of stirring, as it was too great for even an approximate counting of the number of turns per minute. This is easily explained when we consider that the force propelling the liquid increases with the current passing through the solution and also with the increase of strength of the magnetic field. Thus when the cell and the coil are connected in series, this force would be approximately proportional to the square of the current. As a matter of fact the rate of stirring would not rise as fast as this, on account of the rapid increase of friction in the liquid with its increasing speed.

It should also be mentioned that the bottom of the cell is preferably not flat, but V-shaped as shown in the cut, in order that a small amount of mercury may form a complete ring on it. If 40 g. of mercury be used, the total weight of the apparatus will be about 100 g. and so within the capacity of an ordinary balance.

Since the requirement of a motor has been one of the most objectionable features of the rapid methods for electro-analysis, it is hoped that this apparatus by avoiding the use of all moving parts, will facilitate the introduction of these methods into practical work.

UNIVERSITY OF MINNESOTA,
Minneapolis, Minn.
Aug. 20, 1907.

THE RAPID DETERMINATION OF ZINC BY ELECTROLYSIS.[1]

FRANCIS C. FRARY.
Received August 24, 1907.

A great many methods have been proposed for the determination of zinc with the use of stationary electrodes; the use of solutions containing oxalates, citrates, acetates, lactates, formates, cyanides and phosphates being recommended by various authors. The use of a potassium zincate electrolyte is strongly recommended by Amberg[2] who obtained unsatisfactory results with the sodium zincate electrolyte recommended by Millot[3], v. Foregger[4], and others. Spitzer[5] has shown that the sodium zincate method gives good results with a nickel gauze cathode, and that while Amberg required 40 g. of KOH for 0.5 g. zinc, the amount of NaOH required is only a few g., barely enough to give a clear solution.

With a rotating anode, using a silver-plated platinum dish as cathode, Exner,[6] Ingham,[7] and Miss Langness,[8] have obtained concordant results

[1] Also published in Z. angew. Chem.
[2] Ber., 36, 2489 (1903).
[3] Bull. soc. chim., 37, 339.
[4] Dissertation Bern., 1896.
[5] Z. Elektrochem., 11, 391.
[6] This Journal, 25, 896.
[7] Ibid., 26, 1269.
[8] Ibid., 29, 459.

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from a sodium zincate solution containing from 2-12 g. NaOH per 100 cc. Exner and Ingham obtained satisfactory though coarsely crystalline deposits from an acetate solution, and Ingham has also recommended the use of a formate electrolyte. Medway[1] has determined zinc from the well known double-oxalate electrolyte, using a rotating cathode. Price and Judge[2] have obtained results at low temperatures with a simple solution of $ZnSO_4$, containing sodium sulphate. But in order to precipitate the last traces of zinc they found it necessary to cool with ice the funnel containing the solution. Methods for use with the mercury cathode have also been worked out, but will not be considered here.

In the course of a few preliminary experiments on the rapid determination of zinc with my apparatus for electromagnetic rotation of the electrolyte, I found that an acetate solution yielded a coarsely crystalline deposit of metal which, although adherent enough for washing in a dish electrode, was easily brushed off from the more exposed surface of the gauze cathode. Furthermore, a very high voltage was required (17-19 volts for a current of 4-5 amperes) and the electrolyte soon began to boil violently. The formate and oxalate electrolytes were not tried, as it seemed probable that their behavior would be similar to that of the acetate solution. The use of sodium hydroxide was found to give fine precipitates and to require a uniformly low voltage; it was therefore chosen for this investigation, and about 8 g. of alkali were used per 100 cc. of electrolyte.

In all experiments where the electrolyte was rotated (except those in Table 3) a cylindrical cathode of nickel gauze was used; in most of the others a nickel dish was used. After weighing, the zinc was removed from the cathode by treatment with dilute sulphuric acid. The amount of nickel dissolved with the zinc appeared to depend on the strength of the acid and the length of the treatment, and varied in extreme cases from 0.0 to 10.4 mg. The average loss was about 1 mg. per determination. The height of the cathode was 5 cm. in each case, and its diameter was such that it just fitted inside the beaker used.

The anode was a spiral of 1 mm. platinum wire; it was noticed that it slowly became brown by use, so after being used 5 times it was washed, boiled in nitric acid containing oxalic acid to remove any lead peroxide which might be the cause of the color, dried at 100-110° and weighed. The color did not appear to be affected by the acid treatment. After further use as anode in 20 determinations, it was washed again with water, dried and weighed, when a loss of 0.8 mg. was found. Without further treatment it was used as anode in 46 more determinations, then washed again, dried and weighed. This time a loss of 0.7 mg. was found. The anode was then boiled with a mixture of nitric and oxalic acids,

[1] Z. anorg. Chem., **42**, 114; Am. J. Sci., **18**, 180.

[2] Chem. News, **94**, 18, (1906).

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washed, dried and weighed. Its color remained unaltered but it had apparently lost 0.2 mg. During the heating with the acid mixture, it was noticed that, after removing the flame, bubbles of gas were continually disengaged from the wire for some time. As there was found to be practically nothing dissolved, I thought that the platinum oxide, whose presence has been offered as an explanation of the catalytic action of platinum-black, might possibly be the cause of the discoloration.

This oxide, if present, should dissociate at a relatively low temperature, so the spiral was quickly passed through the flame of a blast-lamp. The brown color disappeared at once, leaving the pure white platinum, whose surface appeared a little roughened in comparison to the polished surface of the upper part of the wire, which was new at the beginning of the series of determinations. The spiral was now heated to redness, cooled, and weighed. The loss in weight after heating was found to be 0.5 mg. Another washing with water and alcohol and drying, failed to change the weight. The loss therefore, could not be caused by the difference in the film of water on the wire before and after ignition. Senter[1] has recently investigated the behavior of platinum as anode in acid and alkaline solutions, at a potential however, below that at which gaseous oxygen is evolved. He believes that under these conditions, platinum goes into solution in the presence of acids, as an oxide, while in alkaline solutions he could find no evidence of an oxide in the solution. It would appear possible that in this case the oxide formed by the SO_4 ions at the anode would be prevented from dissolving by the alkali, and so remain attached to the anode[2]. At least, the rate of solution of the anode appears to be so small as to be negligible in ordinary work.

The cover-glasses and sides of the beaker were washed down with a fine spray of water 5 minutes before the end of the electrolysis, or, in cases where the current was reduced for the second part of the analysis, the washing took place immediately after the reduction of the current.

The experiments 1-3, Table 1, and all in Table 4 were conducted in a 150 cc. beaker at a dilution of about 125 cc. and the solution was not cooled. In all other experiments with the magnetic rotation, the electrolyte had a volume of about 100 cc. and was contained in a 125 cc. beaker. This smaller beaker was surrounded by a spiral of lead pipe through which water could be passed, if desired, in order to cool the electrolyte.

On completion of each determination, the current was reduced to about

[1] Trans. Faraday Soc., 2, 142 (1906), (from an abstract in the J. Chem. Soc., 92, 68 (1907)).

[2] Since this article was written my attention has been called by an abstract in the current number of the J. Chem. Soc., 1907, [2] 698, to an article on the electrolytic oxidation of platinum by C. Marie, in Compt. rend., 145, 117 (July 8, 1907). Marie shows that the oxide formed liberates I from KI + HCl, therefore, he considers it to be a peroxide.

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one ampere and the alkaline liquid was drawn off and replaced by distilled water, without breaking the current, care being taken not to expose the zinc deposit to the air till most of the alkali had been removed. The first 200 cc. of the alkaline liquid were reserved for testing, and the washing finished in the usual manner. After rinsing with alcohol the cathode was dried at 100-120°, cooled in a desiccator and weighed.

The alkaline liquid was acidified with sulphuric acid and tested for zinc by the addition of 3-4 cc. of a 10 per cent. solution of potassium ferrocyanide. The test must be allowed to stand 10 minutes if no precipitate appears before that time, as with small amounts of zinc the precipitation does not take place at once. Under these conditions 0.2 mg. of zinc causes a distinct cloudiness in 200 cc. of the solution.

Exner and Ingham obtained concordant results with 5 amperes at 5-6 volts in 15-20 minutes. The average of the results on the same solution seems to have been assumed as correct. In no case do they record that they tested the alkaline liquid remaining after the determination, and the same remark holds true for the later work of Miss Langness and of Medway.

The experiments in Tables 1 and 2 show that one can get concordant results under varying conditions, which results, nevertheless, are uniformly low. In every case zinc could be detected in the liquid drawn off at the close of the determination, If the testing of this liquid be neglected it would seem that the precipitation of the metal was complete at the end of 35-40 minutes.

TABLE 1.

Electrolysis with Magnetic Rotation,[1] Without Cooling. Nickel Gauze Cathode.

No.	Solution	Zinc found	Error (mg.)	Amp.	Volt.	Time (min.)	Temperature at start	Temperature at end	Zinc found in solution after electrolysis.
1	A	0.1965	—1.5	7.4	..	33	cold	...	trace
2	A	0.1968	—1.2	5.9	4.3	34	warm	...	trace
3	A	0.1966	—1.4	5.8	4.4	40	warm	...	trace
4	B	0.0912	—0.9	4.3	..	35	cold	60°	trace
5	B	0.0914	—0.7	4.5	..	50	cold	...	trace
6	B	0.0915	—0.6	6.2	4.	50	cold	90°	(test lost)
7	B	0.0916	—0.5	6.5	3.6	50	cold	91°	none

TABLE 2.

Electrolysis of Solution C with Cooling and Magnetic Rotation of the Electrolyte Nickel Gauze Cathode. Electrolysis Started at Room Temperature.

No.	Zinc found	Error (mg.)	Amp.	Volt.	Time (min.)	Final temperature	Zinc found in solution after electrolysis
1	0.1770	—15.8	4.4	4.4	10	30°	much
2	0.1920	— 0.8	4.5	4.6	15	37°	trace
3	0.1916	— 1.2	4.4	4.6	25	36°	"
4	0.1922	— 0.6	4.5	4.2	31	44°	"
5	0.1925	— 0.3	5.3	4.3	45	50°	"
6	0.1932	+ 0.4	4.5	4.1	51	39°	bare trace

[1] Using my apparatus for rapid analysis by electrolysis, as described in the preceding paper.

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Experiments 4-7 (Table 1) show that with about 5 amperes most of the zinc was precipitated at the end of 35 minutes, but the last traces required 25 minutes more for their removal. The experiments in Table 2 show that under other conditions almost all of the zinc is precipitated at the end of 15 minutes but the last traces are difficult to remove as long as the current density is so high. In comparison with these results the later experiments in Table 5 show the conditions under which the metal may be completely precipitated in 35 minutes.

As it seemed probable that the precipitation of zinc by means of the rotating anode had not been complete in the time given by Ingham and Exner, a series of qualitative experiments were undertaken with a rotating anode and a nickel dish as cathode. For each experiment about 0.2

TABLE 3.

Qualitative Experiments with Rotating Anode and Nickel Dish Cathode. Electrolysis Started at Room Temperature.

No.	Amp.	Volt.	Time (min.)	Final Temperature	Zinc in solution after electrolysis.
1	4.8	4.8	20	40°	much
2	5.	...	17	...	much
3	5.3	4.5	30	...	trace
4	5.3	5.	35	53°	trace
5	4.9	4.8	47	...	bare trace
6	4.9	4.8	57	52°	bare trace

g: zinc as sulphate was used, and 8 g. of sodium hydroxide. After electrolysis the alkaline solution was drawn off and replaced by distilled water without breaking the current. The results are given in Table 3, and indicate that the precipitation with the rotating anode, under the conditions given by the above-named investigators (except that a nickel dish was used instead of a silver-plated platinum dish) could scarcely be complete in less than an hour, and that in this respect the behavior of the solution is the same with the rotating anode as with the magnetic rotation. The failure to test the liquid remaining at the close of the analysis is one which occurs in very many published investigations of electro-analytical methods, and which can not be too strongly condemned.

A very essential condition in the deposition of zinc seems to be the temperature at which the electrolysis takes place. The importance of this factor in alkaline solutions is shown by the well-known fact that such solutions dissolve zinc very readily, and the more readily, the higher their temperature. In the work of Exner, Ingham and Miss Langness, the temperature was not observed nor its influence considered, although with the current and voltage used the solution must have become quite warm. Amberg, working with potassium hydroxide solutions of much higher concentration, found that if the solution was kept continually at a temperature above 60°, the metal had a strong tendency to precipitate in a spongy form. He found that at 40° the precipitate was of good quality

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but that there was no advantage in keeping the solution at that temperature. He, therefore recommends that the solution be heated to 60-70° at the start and then allowed to cool off to room temperature. Spitzer[1] did not study the effect of the temperature, but contented himself with showing that it was unnecessary to heat the solution and that the precipitate obtained at room temperature was very satisfactory. Jene[2], on the contrary recommends a temperature of 50° for the determination.

My experience is in accord with that of Amberg, that at high temperatures the zinc often deposits in a spongy form, and I also find that, at high temperatures, it is very difficult to deposit the last traces of the zinc. With the use of the higher current-density required for rapid deposition, there occurs another difficulty in that the zinc appears to redissolve much more readily than it does at the same temperature with lower current-densities. Therefore, for about 0.2 g. zinc I have found it advantageous to use a current of about 4.5 amperes for 15 minutes, and then continue the electrolysis 15-20 minutes with 1-2 amperes[3].

During this latter interval the temperature also falls perceptibly, as the heat-evolution is much smaller. The experiments in Table 2 show that little, if anything, is gained by using the strong current more than 15 minutes, as at the end of that time all but about 1 mg. of the zinc has been precipitated. The temperature also rises steadily in spite of the cooling. If, however, at the end of the first 15 minutes the current is

TABLE 4.

Electrolysis of Solution A with Magnetic Rotation of the Electrolyte, but without Cooling. Nickel Gauze Cathode. Current Reduced during latter Part of the Analysis. Electrolysis Started at Room Temperature.

No.	Zinc found	Error mg.	Amp. a	Amp. b	Volt. a	Volt. b	Time (min.) a	Time (min.) b	Time (min.) total	Zinc found in solution after electrolysis
1	0.1983	+0.1	5.	1.2	5.7	3.5	15	22	37	none
2	0.1992	+1.0	5.	1.3	..	..	15	10	25	bare trace
3	0.1978	—0.4	5.	1.2	3.9	2.8	15	20	35	none
4	0.1909	—7.3	5.	1.2	..	2.7	17	16	33	much
5	0.1988	+0.6	5.	1.2	..	2.8	15	20	35	none
6	0.1914	—6.8	4.3	1.2	4.1	2.6	18	22	40	much

reduced to 1 to 2 ampere and the electrolysis continued for about 20 minutes, all the zinc is removed, as shown by experiments 1, 3 and 5 in Table 4, and by Table 5. Experiments 2, 4 and 6 (Table 4) show that the reduction of current-density alone, without cooling, does not always give reliable results, while with both cooling and reduction of current-strength (Table 5) the results are very reliable. In all cases where the current used for electrolysis was reduced to 1 to 2 ampere, the current in the

[1] Z. Elektrochem., 11, 391.

[2] Chem.-Ztg. 1905, 803; Z. Elektrochem., 12, 388, (1906).

[3] In the tables the conditions during the first interval are marked *a*, those during the second, *b*.

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solenoid was kept at 4.5-5 amperes by means of an auxiliary circuit, and the rotation of the liquid remained quite vigorous. When only 0.1 g. of zinc is present, the reduction of the current seems to be less necessary (Table 6).

TABLE 5.

Electrolysis of Solution C with Cooling and Magnetic Rotation of the Electrolyte. Current Reduced during Second Part (*b*) of each Determination. Nickel Gauze Cathode. Electrolysis Started at Room Temperature.

No.	Zinc found	Error (mg.)	Amp. *a*	Amp. *b*	Volt. *a*	Volt. *b*	Time (min.) *a*	Time (min.) *b*	Time (min.) total	Final temperature	Zinc found in solution after electrolysis
1	0.1926	—0.2	4.5	1.1	4.6	3.2	17	23	40	23°	none
2	0.1930	+0.2	4.5	1.2	4.6	3.1	20	15	35	31°	none
3	0.1934	+0.6	4.5	1.2	..	..	17	17	34	...	bare trace
4	0.1926	—0.2	4.7	1.7	4.5	3.3	18	18	36	28°	none
5	0.1944	+1.6	4.7	1.7	4.2	3.6	15	20	35	25°	none[1]
6	0.1930	+0.2	4.4	1.7	4.3	3.3	15	17	32	35°	none
7	0.1926	—0.2	4.4	1.7	4.3	3.5	15	17	32	26°	bare trace
8	0.1944	+1.6	4.5	0.9	4.5	3.	25	17	42	22°	none[1]
9	0.1930	+0.2	4.5	0.9	4.3	..	15	17	32	28°	bare trace

[1] Nos. 5 and 8 were precipitated on a rough cathode, were dark-colored and probably oxidized.

TABLE 6.

Electrolysis of Solution B with Cooling and Magnetic Rotation of the Electrolyte. Nickel Gauze Cathode. Electrolyte at Room Temperature at the Beginning of each Determination.

No.	Zinc found	Error (mg.)	Amp.	Volt.	Time (min.)	Final temperature	Zinc found in solution after electrolysis
1	0.0902	—1.9	5.3	4.6	30	52°	trace
2	0.0908	—1.3	4.3	4.4	25	41°	trace
3	0.0920	—0.1	4.3	4.1	30	...	none
4	0.0924	+0.3	4.5	4.5	30	...	none
5	0.0920	—0.1	4.5	..	30	...	none
6	0.0924	+0.3	4.5	..	32	47°	none
7	0.0910	—1.1	4.5	..	35	45°	trace
8	0.0912	—0.9	4.4	4.6	32	38°	none

TABLE 7.

Electrolysis of Solution A with Nickel Dish as Cathode without Cooling or Rotation of Electrolyte. Solution Heated to 40-60° before Electrolysis.

No.	Zinc found	Error (mg.)	Amp.	Volt.	Time (min.)	Zinc found in solution after electrolysis
1	0.1973	—0.9	1.05	3.15	165	none
2	0.1986	+0.4	1.1	2.95	165	none
3	0.1978	—0.4	0.95	3.5	180	none
4	0.1985	+0.3	0.95	...	180	none
5	0.1990	+0.8	0.8-1	...	135	none[1]

[1] Nickel gauze cathode used.

To show that the rapid method gives results agreeing with those from the ordinary determination, the 5 analyses given in Table 7 were made, using a nickel dish as cathode. The mean of these results is 0.1982 g.

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zinc; the mean of the only rapid analyses of solution A where the precipitation was complete (Nos. 1, 3 and 5, Table 4) is 0.1983 g. In the case of the other solutions (B and C) the mean of all the determinations where complete precipitation was assured (except Nos. 5 and 8, Table 5), was assumed to be the correct value and the error calculated on this basis.

The deposit was generally of a fine steel-gray color and metallic luster. It was noticed that the character of the precipitate is very dependent on the surface of the cathode; on one cathode which had been treated for a long time with acids and thus had its surface roughened, the precipitate was always of a dark color and had a tendency to oxidize, as shown by experiments 5 and 8 (Table 5), where this cathode was used.

Summary.

1. With electromagnetic rotation of the electrolyte 0.1 g. zinc can be completely precipitated by 4.5 amperes in 30 minutes on a nickel gauze cathode. About 8 g. of sodium hydroxide should be used, and the electrolysis should be conducted at as low a temperatue as possible.

2. For quantities of zinc up to 0.2 g. the current-strength should be 4-5 amperes for 15 minutes and then about 1.5 amperes for 20 minutes. (Other conditions are the same as in 1).

3. The testing of the liquid remaining after electrolysis is essential.

4. It is highly improbable that complete precipitation of 0.2 g. zinc can be obtained with 5 amperes in 15-20 minutes, as stated by Exner and Ingham. From the results obtained it would also seem improbable that the concordant results obtained by Miss Langness with 10-13 amperes in 3 minutes represent complete precipitation.

The work on which this and the preceding articles are based was done during the spring and summer of 1907 in the electro-chemical laboratory of the Royal Technical High School at Berlin. I take this occasion to thank Professors von Knorre and Peters, and Dr. Arndt, of that laboratory, for their interest in this work and the many kindnesses shown me during its course.

UNIVERSITY OF MINNESOTA,
Minneapolis, Minn.,
Aug. 20, 1907.

CLAY ANALYSIS—AN EXAMINATION OF THE RESIDUE LEFT AFTER VOLATILIZATION OF THE SEPARATED SILICA WITH HYDROFLUORIC AND SULPHURIC ACIDS.

First Paper.

BY W. R. BLOOR.

Received August 5, 1907.

It has been generally assumed that the residue left after volatilization of the separated silica with hydrofluoric and sulphuric acids in the ordinary process of clay analysis is composed of iron and aluminium oxides and as such is to be added in with them.

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With the view of testing the correctness of this assumption, an examination was made of a number of these residues, obtained in the course of a series of analyses of clays of the State of Washington. The method used in separating the silica was that outlined in Bulletins 176 and 305, U. S. Geol. Survey, special precautions being taken to ensure complete fusion. From 6-8 g. of sodium carbonate per gram of clay were used and the fusion was continued with frequent rotation of the crucible for fifteen minutes after the melt was quiescent. The silica was obtained by double evaporation (to approximate dryness except in Nos. 1, 5, 7 and 10, which were allowed to dry for three hours at 125°), with intervening filtration, and washed until the washings gave no cloudiness with silver nitrate solution. After blasting to constant weight, it was moistened with water and sulphuric acid and volatilized with hydrofluoric acid. The weighed residue was fused with potassium bisulphate and taken up with water and a little sulphuric acid. Any residue was filtered off and weighed as insoluble matter. Fe_2O_3 and Al_2O_3, etc., were determined in the usual manner. CaO was obtained by double precipitation. The first precipitation was generally slow and was allowed a day or so to complete. The precipitate was filtered off, dissolved in dilute hydrochloric acid and reprecipitated, the second precipitation taking place immediately. MgO was obtained as usual. TiO_2 was found in all cases where it was present in the clay, but was not determined. Blanks were run for all reagents.

All the samples mentioned in the following table were ordinary clays with the exception of Nos. 10 and 11, which were argillaceous limestones.

The average composition of the residue as drawn from the accompanying table is: Fe_2O_3, Al_2O_3, etc., (precipitable by ammonia in presence of ammonium salt) 57.36%; CaO, 21.48%: MgO, 14.05%. The residue averages 1.01% of the separated silica.

In Nos. 1, 5, 7 and 10 the mass was allowed to dry for three hours on a hot plate at 125° with the result that while there was an increase in the total residue of about 40% the amount of Fe_2O_3 and Al_2O_3 was increased only about 7%. Later experiments also go to show that drying at this temperature does not materially increase the amount of Fe_2O_3 and Al_2O_3 in the residue.

When the residue compared with the silica is large (Nos. 1, 2, 3, 5, 7, 10 and 11) the percentage of Fe_2O_3 and Al_2O_3 present, is larger, but not markedly so (increase of 4½%).

When the per cent. of CaO is high in the original sample (Nos. 3, 4, 8, 9, 10, 11, 13, 14, 16, 17, 20, 21 and 22—averaging 2.01%) the percentage of Fe_2O_3 and Al_2O_3 in the residue is lower (decrease of 4%), while the percentage of CaO is somewhat higher (7% increase), than the average.

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No.	Silica content of 1 gm. of clay	Total residue by weight	Al_2O_3 etc.	Fe_2O_3	Al_2O_3, Fe_2O_3 % total residue	CaO	CaO % total residue	MgO	MgO % total residue	Residue insoluble in $KHSO_4$, H_2SO_4	Total residue by addition	Residue % of original SiO_2	No.
1	0.5324	0.0072	0.0023	0.0008	43.66	0.0007	9.72	0.0022	30.55	0.0006	0.0071	1.35	1
2	0.5724	0.0062	0.0006	0.0020	41.94	0.0005	8.06	0.0014	22.58	0.0007	0.0052	1.08	2
3	0.6374	0.0080	0.0018	0.0020	54.30	0.0020	28.57	0.0007	10.00	0.0005	0.0070	1.02	3
4	0.6244	0.0036	0.0000	0.0010	30.00	0.0004	12.12	0.0014	42.12	0.0009	0.0033	0.58	4
5	0.5260	0.0074	0.0028	0.0018	64.00	0.0020	28.17	0.0000	0.00	0.0005	0.0071	1.40	5
6	0.5703	0.0046	0.0006	0.0018	52.17	0.0013	22.73	0.0000	0.00	0.0005	0.0042	0.80	6
7	0.6144	0.0080	0.0025	0.0031	71.80	0.0008	10.25	0.0012	15.38	none	0.0078	1.30	7
8	0.5496	0.0040	0.0020	0.0014	83.00	0.0007	17.07	0.0000	0.00	"	0.0041	0.73	8
9	0.5964	0.0051	0.0029	0.0010	88.63	0.0000	0.00	0.0005	11.36	"	0.0044	0.85	9
10	0.1434	0.0078	0 0025	0.0039	80.00	0.0011	13.75	0.0005	6.25	"	0.0080	5.40	10
11	0.1420	0.0037	0.0005	0.0029	76.44	0.0008	17.77	0.0003	6.60	"	0.0045	2.60	11
12	0.8076	0.0027	0.0014	0.0000	53.85	0.0009	34.60	0.0006	11.54	"	0.0026	0.33	12
13	0.5876	0.0028	0.0006	0.0000	20.69	0.0017	58.62	0.0005	20.69	"	0.0029	0.48	13
14	0.5787	0.0013	0.0000	0.0000	0.00	0.0012	70.59	0.0005	29.41	"	0.0017	0.22	14
			0.0024									0.54	15
15	0.7455	0.0043			60.00	0.0010	25.00	0.0006	15.00	"	0.0040		
16	0.5805	0.0027	0.0010		40.00	0.0008	32.00	0.0004	16.00	0.0007	0.0029	0.46	16
17	0.6249	0.0019	0.0010		43.42	0.0013	56.52	0.0001	0.43	none	0.0023	0.30	17
18	0.5660	0.0036	0.0029		85.30	0.0002	5.88	0.0003	8.82	"	0.0034	0.68	18
19	0.6612	0.0020	0.0020		100.00	0.0000	0.00	0.0000	0.00	"	0.0020	0.30	19
20	0.6324	0.0050	0.0043		93.48	0.0003	6.52	0.0000	0.00	"	0.0046	0.79	20
21	0.6316	0.0026	0.0011		37.93	0.0013	44.83	0.0005	17.24	"	0.0029	0.41	21
22	0.6186	0.0038	0.0015		41.66	0.0005	13.88	0.0016	44.44	"	0.0036	0.61	22

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Taking the results as a whole and in spite of the fact that the quantity of material in each case is small, and the liability to error, consequently great, the average results show a suprising constancy and justify the conclusion that in the analysis of clay by the method outlined above, the silica so separated is contaminated to some degree by the main constituents of the clay. The amount of contamination by substances other than Fe_2O_3 and Al_2O_3 is however, except in extreme cases, so small that it may be neglected unless extreme accuracy is required.

W. F. Hillebrand[1] states as follows: "Quite as rarely (as barium) is calcium or magnesium ever a component of the residue, if the decomposition of the rock powder was complete at the outset." Since the results obtained differ almost entirely from this statement, it was thought well to consider some of the possibilities of error in the experiment. The main ones may be summed up as follows: (1) insufficient washing of the separated silica; (2) incomplete decomposition of the clay at the outset; (3) evaporation in porcelain may have induced contamination; (4) different action of clay and rock powder in fusion or subsequent treatment. The first two may be dismissed as following in the main the general usage in silicate analysis. The third possibility was made the subject of a second series of experiments. A sample of ordinary clay was taken and prepared very carefully. After fusion in the regular way duplicate samples were evaporated in porcelain (Royal Berlin) and in platinum dishes, the silica volatilized and the residues analyzed as before. The results as yet are not sufficiently definite to throw any light on the point in question.

PULLMAN, WASH.

THE CONSTANTS AND VARIABLES OF THE PARR CALORIMETER.

BY S. W. PARR.

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The calorimeter using sodium peroxide as a medium of combustion was first described in the October number of this Journal[2], 1900.

The chief element in the process as outlined at that time was the establishment of the ratio between the true heat of combustion of the fuel used and the total heat of the reaction developed by the process. For example, if the total indicated heat of a hydrocarbon, burning in a closed chamber by means of sodium peroxide were found to be 10,000 calories, then the true heat of combustion would be 7300 calories, and the other 2700 units would represent the heat of combination of the carbon dioxide and water with the chemical employed. The constant, therefore, representing the part of the reaction which was to be credited to combustion, was 73 per cent. This factor was determined empirically

[1] Bull., 305, U. S. Geol. Survey, 80.

[2] This Journal, 22, 646.

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by comparison with results on the same material under the same conditions as obtained by means of the Mahler-Atwater apparatus. Moreover, as the ratio seemed to hold good for semibituminous coals as well as for coals of the highly bituminous type, it was assumed that this ratio was the correct one whether the excess of heat was due to the absorption of carbon dioxide or of water, and that fuels varying in the relative amounts of hydrogen and carbon were adapted for use by this process. Here, again, the basis for the conclusion was empirical.

In subsequent experiments, where a wider range of fuels was available, more especially such coals as were common to the continent of Europe, a lack as to the completeness of combustion was noted, and it was sought by means of the addition of other chemicals to increase the oxidizing effect of the sodium peroxide in order to insure a uniform and complete reaction. The materials tested were of two types: first, other organic substances of constant composition, such as sugar, tartaric acid, etc., which were added on the principle that kindling wood added to a fire helps to consume the more refractory material, and second, superoxidized compounds like barium peroxide, niter, potassium persulphate, etc., which were added to test the effect of substances more ready to part with their oxygen than does the sodium peroxide, and perhaps establish a condition where nascent oxygen might be present. Both of these ideas seemed to have some proper basis, and application was made of the same by proposing a mixture of tartaric acid one part, and potassium persulphate two parts, as an intensifier or accelerator of combustion.

On the basis of this second series of experiments upon European coals which were carried on in Dr. Lunge's laboratory at Zürich, a number of articles have appeared more or less critical of the process. Dr. Lunge, the first[1] and the last[2] to contribute to this discussion, has defended it as being well adapted to technical work. Langbein[3] bases his criticism on the results obtained by Lunge and Offerhaus[4] on the theory that variable temperatures gave varying degrees of completeness of combustion, and hence an inherent unreliability would attach to the values.

Further experiments by Lunge and Grossman[5] and by Constam and Rougeot[6] were mainly devoted to the influence of varying qualities of the sodium peroxide and to the fineness of division of that material.

While the specific answer to these criticisms is to be found in the presentation of facts and the discussion which follows, it may be said as a general proposition, first, that any results based upon the use of sodium

[1] Z. angew. Chem., 14, 800 (1901).
[2] Ibid., 19, 1963 (1906).
[3] Ibid., 16, 1073.
[4] Ibid., 16, 911.
[5] Ibid., 18, 1250.
[6] Ibid., 19, 1796.

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peroxide which has been sifted or ground or otherwise handled in any manner to permit of the absorption of moisture from the atmosphere, are open to question. The slow absorption of moisture by sodium peroxide results in the formation of $Na_2O_2.2H_2O$[1], and this compound at the higher temperature of fusion forms sodium hydroxide with evolution of heat.

Second, the adverse conclusions are all based upon combustions in which an indefinite amount of unburned carbon remained from the reaction. The extra chemicals used to accentuate the oxidizing effect of the sodium peroxide were tartaric acid and potassium persulphate, either separately or in conjunction. The fact that unburned carbon remained in small amounts from the use of this material, and further that the variables under discussion ranged within narrow limits, approximately from one to three per cent., would seem to indicate that the first essential in any critical study of the process would be to first eliminate or account for the unburned portion of the charge.

Under the first proposition, that of the effect of absorbed moisture, an easy verification of the fact of an increase of temperature is shown as follows: Ten g. of sodium peroxide were poured upon a watch glass and exposed to the air of the laboratory for about one hour. The amount of moisture taken up as shown by increase of weight was approximately 0.5 g. This material was then employed in a combustion under standard conditions, so that comparison could be made with the rise in temperature where the sodium peroxide had not been exposed to moist air. The following results were obtained:

TABLE 1.

EFFECT OF ABSORBED MOISTURE.

Sodium Peroxide used.	Combustible.	Total rise in Temperature.	Average rise.
10 g. Na_2O_2 + 0.45 gram H_2O	0.5 g. Benzoic acid.	2.377	2.374
10 g. Na_2O_2 + 0.44 gram H_2O	0.5 g. Benzoic acid.	2.370	
10 g. Na_2O_2 without H_2O	Average of 8 tests.	2.180	2.180

Excess of temperature due to absorbed H_2O, 0.5 g.....0.194

Concerning the higher values resulting from the use of sifted material, it was suspected that either in the process of manufacture or in sifting the peroxide, the finer portions would absorb relatively more than the coarse, and it was a direct result of this behavior of the finer material that the tests recorded in the above table were made. Further experience in this same line demonstrated the fact that a certain procedure was necessary in the manufacture and handling of the sodium peroxide. By arrangement, therefore, with the manufacturers, a special burning of sodium is made to produce a peroxide which shall be as nearly as possible free from absorption of both water and carbon dioxide. This product is hermetically sealed in tins of such a size that the entire contents of a tin may be emptied at once into the glass container from which it is to

[1] J. Chem. Soc., 14, 267.

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be used. By a process of manufacture, therefore, conducted with special care to accomplish a prescribed end, and by bringing this material to the laboratory in unbroken packages, it has been possible to readily provide a product of remarkable uniformity as has been shown by a continuous series of tests, extending through the last four years, since such material was available.

One thing further should be noted in this connection. A very important feature of the case is the kind of retainer in which the user keeps his current supply of sodium peroxide and from which he measures his portions for the tests. The avidity of the material for moisture requires a container with perfect seal. The best obtainable ground glass stoppered bottles were found altogether useless for this purpose. Various types of jars were tried, but none have served the purpose in a satisfactory manner, except one having a lever clamp known as the "lightning" or "Putnam" jar.

In this connection a comparison was made between the material as above prepared and some peroxide prepared without such definite specification, bearing the label of Dr. Heinr, Koenig & Company, Leipzig, Germany.

TABLE 2.

COMPARISON OF AMERICAN AND GERMAN SODIUM PEROXIDE.

Material	Rise in temperature
Na_2O_2 from Standard Calorimeter Co.	Average of 8 tests.....2.180
Na_2O_2 from Koenig & Co., Germany.	Same.....2.223
	2.213 Average 2.218
Higher reading of German peroxide	0.038°

For variable or unknown sodium peroxide there is indicated, therefore, the necessity of standardizing the material in order to determine its quality and effect when used in combustions. This, of course, necessitates a definiteness in all the other conditions and the elimination of any variable which might arise from incomplete combustion, etc. This, as will be shown in what follows, is a comparatively simple proposition and brings us to a discussion of the second topic, *viz.*:

The Use of Intensifiers for Producing Completeness of Combustion.

Reference has been made above to the use of additional chemicals to produce a more complete combustion than could take place with sodium peroxide alone. It must be apparent that a complete combustion of material is necessary before any exact study of the process could be undertaken. While tartaric acid and potassium persulphate made the best mixture of any substance studied up to that time, further improvement was possible and upon this part of the work much time and experiment has been spent.

Accelerators.—The accelerators employed have covered a very wide range of material. They naturally fall into certain groups, as, for ex-

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ample, those producing additional heat by reason of their own fuel value, such as organic acids, sugar, powdered magnesium, etc. In this class also might be placed ammonium salts, for in these compounds the hydrogen burns, liberating nitrogen. Ammonium chloride and ammonium phosphate were quite extensively tried. Among these also may be mentioned ammonium persulphate which, in addition to furnishing heat from its own reactions with sodium peroxide, liberated also considerable oxygen. A number of other substances furnishing practically nothing but easily accessible oxygen were niter, potassium chlorate, peroxides of barium, calcium, zinc, lead, etc. There was also tried sodium perborate, but as the same effect could be accomplished by means of boric acid, that material was used instead.

It is needless to go into the details of these very numerous and extended tests. In general, those compounds which contain in their structure or develop from the reaction any considerable amount of water are to be discarded, because the benefit derived is small, while the pressure developed from the liberated oxygen may make, with sufficiently high temperature, too great a strain upon the bomb.

Mixtures containing boric acid make a very satisfactory fusion with bituminous coals, but not with anthracites. Moreover, the avidity of the finely divided boric acid for moisture makes it variable, as to its own heat value, requiring standardization for each new lot of material.

The accelerators finally found to be of greatest efficiency were (a) a mixture of potassium and ammonium persulphates in the ratio of two to one, and (b) potassium chlorate alone. By use of these substances a uniformly complete combustion is attainable. This statement should be qualified only to this extent. Sugar-carbon, anthracite and similarly difficultly combustible substances should be ground to pass a 200-mesh sieve, or, what is quite as convenient, filter off on a Gooch crucible the unburned portion, weigh and deduct the same from the amount of the charge. Account can thus be made of particles that adhere to the surface of the chamber and about the terminals in the upper part of the bomb above the zone of fusion. Such material, while extremely minute in amount, should be taken account of in any investigation looking to the establishment of factors or evidence of accuracy of the process.

With these conditions established as a preliminary requisite, we may take up, first, the verification of the most important constant involved in the process, *viz.* : the *Ratio of 73 per cent.* as representing the part the heat of combustion is of the total heat evolved.

The Reaction Constant of 73 Per Cent.

The first essential in studying the adaptability of sodium peroxide as a medium of combustion is to determine the behavior of both carbon and hydrogen with respect to the heat evolved in combining their combustion products with the chemical employed. That is, if carbon dioxide in

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uniting with sodium peroxide has a ratio of heat to the total heat evolved which is widely different from the ratio found where water is the uniting substance, then the process as a method for measuring heat values is without application except upon substances of known or constant composition with respect to their carbon and hydrogen content. On the other hand, if these respective heat ratios are identical or vary within sufficiently narrow limits, then all hydrocarbons, however, widely varying in their amounts of carbon and hydrogen, may indicate their heat of combustion by applying this constant to the total heat indicated in the reaction.

It may be well, first, to present some of the earlier data obtained in attempting to find these two ratios. The plan followed was to first determine the factor for carbon alone, by use of pure sugar-carbon, and for the hydrogen factor, make use of a pure hydrocarbon, as naphthalene, in which the carbon values having been determined, the factor for hydrogen could be directly deduced.

In some earlier experiments conducted in 1902 eight combustions of pure sugar-carbon gave an average for the total indicated heat of 11021 calories. If we accept 8080 as the correct factor for carbon, we have a ratio $\frac{8080}{11021}$ or expressed in per cent. of 73.3. The carbon employed was carefully prepared by finally heating in a current of chlorine gas with subsequent washing in alkaline and acid water, with final washing with pure water.

For the hydrogen factor, pure naphthalene was prepared by repeated crystallizations from alcohol. It was found impossible to burn this material satisfactorily without an additional chemical. For this, the mixture of ammonium and potassium persulphate was used, one of ammonium persulphate to two of potassium persulphate. It was necessary first to standardize the persulphates used in order to determine the heat correction that should be applied to these chemicals. This was accomplished by making a series of combustions with a given quantity of naphthalene (0.2 g.) and varying the persulphate as in the following table. The total rise in temperature is given in degrees centigrade.

TABLE 3.—STANDARDIZATION OF PERSULPHATE ACCELERATOR.

Chemical constants	1 gram persulphate	1.5 grams persulphate	2 grams persulphate	2.5 grams persulphate
		Total Rise in Temperature		
Approximately	1.634	1.827	2.022	2.214
10 grams	1.635	1.828	2.022	2.220
(measured)	1.636	1.829	2.024	2.222
of Na_2O_2 and	1.636	1.830	2.025	2.216
0.2 grams		1.837	2.028	2.229
pure naphthal-		1.838	2.030	2.231
ene, $C_{10}H_8$.		1.839	2.030	2.233
			2.032	2.241
Average	1.635	1.832	2.026	2.225
Difference		0.197	0.194	0.199
Average of Differences		0.197		

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It would seem from the foregoing table that the proper correction for the persulphate mixture would be 0.197° per 0.5 g. By applying, therefore, this correction in the same series of readings, we have the indicated heat for naphthalene. The true combustion factor for naph-

TABLE 4.

COMBUSTION CONSTANT FOR NAPHTHALENE.

Persulphate Mixture.	Amount of Naphthalene $C_{10}H_8$	Total Rise: Corrected for Radiation	Average Total Rise.	Corrections for Accelerator.	Corrected Temperature.	Total Indicated heat per Kilo. $\frac{tx2135}{wt}$	Ratio of 9592 to total heat.
		1.634					
		1.635					
1 gr.	0.2	1.636	1.635	0.384	1.241	13250	73.1
		1.636					
		1.827					
		1.828					
		1.829					
1.5	0.2	1.830					
		1.837	1.832	0.591	1.241	13250	73.1
		1.838					
		1.839					
		2.022					
		2.022					
		2.024					
2.0	0.2	2.025	2.026	0.788	1.238	13220	73.3
		2.028					
		2.030					
		2.030					
		2.032					
		2.214					
		2.220					
		2.222					
2.5	0.2	2.216	2.225	0.985	1.240	13240	73.2
		2.229					
		2.231					
		2.233					
		2.241					
		2.313					
		2.319					
		2.327					
2.0	0.25	2.336	2.333	0.788	1.545	13190	73.4
		2.337					
		2.339					
		2.340					
		2.350					
		2.527					
		2.525					
		2.522					
2.5	0.25	2.528	2.531	0.985	1.546	15200	73.4
						Average.....	73.25

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thalene has been taken as 9692, and the ratio is derived by dividing this number by the total indicated heat for the naphthalene. The results are serially arranged in order to show at a glance the highest and lowest results obtained in the various tests.

We have now two sets of results, one for carbon alone, showing an average constant of 73. per cent. for the heat of combustion and the other for naphthalene (composed of 93.75 per cent. carbon and 6.25 per cent. of hydrogen), showing a constant of 73.2 per cent. for the ratio between the actual heat of combustion and the indicated heat of the reaction.

The results of Table 4 were obtained in 1905 by Mr. C. H. McClure, and much credit is due him for the painstaking care with which he carried out that work. A room under temperature control was used and corrections for radiation were applied in all of the tests. There would seem to be from this data, therefore, a close agreement between the heat developed from absorption of carbon dioxide and of water.

To the above results should be added others obtained during the current year by Mr. W. F. Wheeler.

This additional series is given for the reason that in connection with the coal work for the Illinois State Geological Survey a careful examination of methods, appliances and material used in that work was made for the elimination of errors. Results obtained, therefore, in comparison with the Mahler-Atwater apparatus would have still greater value than any preceding.

It may be worth while to refer briefly to some of the points covered in attempting to arrive at correct standards. The oxygen bomb used was of the Atwater type with platinum lining. The water equivalent was sought by burning pure naphthalene. A new lot of this material with Merck's label, highest standard of purity, etc., was obtained. The water equivalent indicated by burning the material was higher than the factor previously established for the calorimeter. An examination of the naphthalene showed that it contained 0.16 per cent. of sulphur. A supply of Kahlbaum's naphthalene was then tested, and it was found to contain 0.13 per cent. of sulphur. After an extended series of crystallizations from alcohol, this difficulty was remedied. But the experience is worth noting, because of the statement occasionally met with recommending naphthalene for this purpose, because of the ease with which this material may be obtained in the pure state. Perhaps a more difficult problem is to decide upon an acceptable factor for naphthalene. Atwater[1] uses a value of 9628 calories. Prof Lord[2] uses 9692. Landolt and Bornstein (1905) gives 9701. Here is a difference of 74 calories in 9600 or over

[1] This Journal 25, 693.

[2] Report of Coal Testing Plant, U. S. Geol. Sur. Prof., Paper No. 48, 180.

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0.70 per cent., sufficient to make a difference of approximately 20 cc. in the water equivalent of the apparatus. A greater variation exists in the values for sugar. The values for benzoic acid are less variable. By elaborating a series of tests with these three substances a water value was established of 445, as against an earlier value of 420, using for the smaller factor, however, a value of 9628 calories for naphthalene. The water equivalent of the other form of calorimeter was obtained first by calculation; all parts being of brass, having a constant composition of zinc, copper and two per cent. of lead, the specific heat of the alloy was taken as 0.092. The total weight of metal being 1470 grams, the calculated equivalent of the metal would be 135 cc. A second method was employed, using the electrical process of Magie-Pfaundler[1]. Three results by this method gave values of 134.8, 135.4, and 135.2, with an average of 135.1. The accepted factor, therefore, was taken as 135, or a total water equivalent in operation of 2135 grams.

Concerning the preparation of pure carbon, crystals of rock sugar were used. As a means for fine grinding, a sample of 100 grams of the carbon was placed in an Abbé ball mill having a jar of Royal Berlin porcelain. After two hours running, the pulverized material was found to have an ash content of 3.16 per cent, indicating a serious wearing of the porcelain. A different method of grinding, was of coürse, necessary. It should, moreover, be noted that the avidity of sugar carbon for moisture makes it necessary that this constituent be removed or taken account of in standardization tests.

On account of the possible variables connected with sugar-carbon, it was deemed simpler to omit the treatment with chlorine gas and depend for a comparison upon the value as indicated by the Atwater bomb. Even if pure carbon were assumed to be obtained, it would still be an open question whether we should accept for comparison the calorific value by Thomsen of 8080 or that of Berthelot of 8137.5. In the table following, the accelerator employed in the combustion was chlorate of potash instead of the persulphate mixture. This has the advantage of being more easily prepared, more constant as to composition, non-hygroscopic and non-deteriorating. Moreover, it has even a higher oxidizing power than the persulphate mixture with a lower correction for its heat of decomposition, thus lessening the possible error in correcting for its own heat equivalent. Contrary to what might be expected, no oxygen is set free in its use, hence it has greater safety so far as danger of explosion is concerned than any other accelerator used. This will be more fully explained under the discussion of the heat equivalent of potassium chlorate. The correction factor employed for 0.5 g. of this accele-

[1] Phys. Rev., 1902.

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rator was 0.040° and for 1. g. 0.108°. The obtaining of these values will also be taken up later in the discussion.

TABLE 5.

COMBUSTION OF SUGAR-CARBON, USING 10 GRAMS Na_2O_2 AND 0.5 GRAM $KClO_3$.

Carbon, less Moisture & Ash	Unburned carbon	Carbon burned	Total Rise, Corrected for Radiation	Correction for Chlorate, Wire & Moisture 0.040+0.008+0.006	Corrected Rise	Total Heat per Kilo $\frac{tx2135}{C. burned}$	Ratio of Bomb value to total heat $\frac{8218}{total\ ht.}$
0.4856	0.0201	0.4655	2.515	0.054	2.461	11,280	72.8
0.4856	0.0159	0.4637	2.541	0.054	2.487	11,310	72.65
0.4856	0.0150	0.4706	2.538	0.054	2.484	11,265	72.95
0.4856	0.0138	0.4718	2.550	0.054	2.496	11,290	72.75
					Average	11,286	72.8

Under corresponding conditions by the same operator combustions of naphthalene were made. Potassium chlorate was used as the accelerator. Relatively more of the naphthalene could be burned than with the persulphate mixture, 0.3 g. giving a good combustion. The following results are tabulated with reference to the ratio of the true heat of combustion, to the total heat indicated for this material.

TABLE 6.

COMBUSTION OF NAPHTHALENE, USING 10 GRAMS Na_2O_2 AND ONE GRAM $KClO_3$.

Naphthalene used	Chlorate used	Total Rise Corrected for Radiation	Correction for Chlorate and Wire 0.108+0.008	Corrected Rise	Total Heat per Kilo: $\frac{tx2135}{wt.}$	Ratio of Naphthalene to total heat: $\frac{9692}{total\ heat}$
0.3	1.0	1.988	0.116	1.872	13,320	72.70 per cent.
0.3	1.0	1.986	0.116	1.870	13,310	72.80
0.3	1.0	1.987	0.116	1.871	13,315	72.75
0.3	1.0	1.967	0.116	1.851	13,160	73.50
0.3	1.0	1.970	0.116	1.854	13,190	73.40
0.3	1.0	1.972	0.116	1.866	13,220	73.30
				Average	13,253	73.1 per cent.

It would seem from all the above results that empirically, at least, the ratio of the heat of absorption for carbon dioxide is the same as for water, that is, the water which forms as a result of the reaction. Reference has been made above to the empirical nature of this factor. This feature has also been made the basis for some of the criticisms concerning the process. At the time of developing the earlier results no factor was available for the heat of composition of sodium peroxide. A factor is now given by De Forcrand[1] of 119.8 per g. molecule. It is of interest, therefore, to calculate these two ratios, using the above factor. The reaction with carbon is,

$$2\ Na_2O_2 + C = Na_2CO_3 + Na_2O.$$

From this we have, expressing the final factor in kilo-calories :—

[1] Compt. rend., 128, 1449.

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$$\frac{(100.3 + 272.6) - 2(119.8)}{12} = 11.108.$$

The theoretical factor, therefore, for the total heat evolved in the reaction is 11.108 calories per kilo. The ratio of 8080, the combustion factor used for carbon to this value, would give a constant of 72.74 per cent.

Calculating in a similar manner for hydrogen, we would have

$$Na_2O_2 + Na_2O + O + 4H = 4NaOH.$$

From this reaction we would have slightly varying results depending upon the factors employed. Using Thomsen's value of 101.9 for NaOH we would have

$$\frac{4(101.9) - (119.8 + 100.3)}{4} = 46.875.$$

Developing the ratio with 34460 as the factor for hydrogen, we have $\frac{34460}{46.875} = 73.5$. If instead of Thomsen's factor we use Berthelot's for NaOH of 102.7, we shall have

$$\frac{4(102.7) - (119.8 + 100.3)}{4} = 47.675$$

and this referred to the hydrogen factor of 34460, gives a percentage for the latter 72.3.

It is no part of the purpose of the present paper to settle points of difference between Berthelot and Thomsen. If we may venture to average the two results, however, we would have 72.9 as the percentage factor for hydrogen. The experimental data, it may be noted, is not more widely at variance than the two authorities above quoted.

Benzoic Acid.—In all of the experimental work, it has been evident that a standard substance was very desirable which would give good fusions and serve as a basis of comparison. Naphthalene has some disadvantages, chiefly because only a small amount may be burned satisfactorily, and small errors are multiplied. Benzoic acid has many points of advantage, but a question arises as to how we shall account for the heat of the water formed from the oxygen of the benzoic acid when this water unites with the sodium peroxide. This heat, of course, can not be credited to combustion in the ordinary sense and hence must be corrected for in the temperature readings.[1] A correction factor of 0.097° is

[1] From tables 4 and 6 we may develop the expression $\frac{34460}{0.73} = 47205$ as representing the heat which would result from the combustion and absorption of water formed from one kilo of hydrogen. One-ninth therefore of 47205—34460 would represent the absorption value per kilo of water. The water equivalent of the system being 2135, it follows that the absorption value per kilo of water divided by 2135 would give the rise in temperature per g. in the apparatus used, that is 0.663°. The empirical factor 0.097° would represent a quantity of water equal to 29.5 per cent. of the benzoic acid used or the equivalent of two molecules.

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used per 0.5 gram of the substance for the heat of this part of the reaction.

Applying this correction, therefore, in a series of combustions of benzoic acid, using ½ g. with ½ g. of potassium chlorate as in Table 5, we have the results as given in Table 7. In selecting a factor for benzoic acid with which to compare the results, it should be noted that Stohman gives one factor of 6281, another of 6360. Stohman and Langbein give 6322. Berthelot and Luginni give 6335. The latter factor has been taken for comparison.

TABLE 7.

COMBUSTION OF BENZOIC ACID, USING ONE-HALF GRAM WITH ONE-HALF GRAM $KClO_3$.

Total rise corrected for radiation	Correction for water formed, reaction-accelerator and wire 0.097 0.040 0.008	Corrected temperature	Total indicated heat $\frac{tx2135}{0.5}$	Indicated calories	Compared with 6335
2.176	0.145	2.031	8675	6330	— 5 cal.
2.180	0.145	2.035	8690	6340	+ 5
2.180	0.145	2.035	8690	6340	+ 5
2.185	0.145	2.040	8715	6360	+25
2.170	0.145	2.025	8645	6315	—20
2.198	0.145	2.053	8780	6410	+75
2.162	0.145	2.017	8610	6280	—55
2.186	0.145	2.041	8720	6365	+30
		Average		6330	—5

Combustion of Other Organic Compounds.—Before leaving the subject of benzoic acid reference should be made to other organic compounds, containing oxygen. In the case of sugar, for example, it is evident that Dulong's formula does not apply. By that procedure the value for sugar would be only 3402 calories instead of 3962 calories, the observed value. By the same argument, the amount of water of composition suggested by the Dulong formula would be inadmissable as a basis for correcting for that constituent. In the following tests, the empirical correction used for this part of the reaction is 0.139° when the amount of sugar is 0.5 g. and 0.167° with 0.6 g.

TABLE 8.

COMBUSTION OF CANE SUGAR WITH 10 GRAMS Na_2O_2 AND ONE GRAM $KClO_3$.

Amount of sugar taken	Correction for hydroxyl reaction	Total correction including chlorate and wire .108 .008	Total Rise	Corrected Rise	Indicated calories $\frac{tx2135x.73}{\text{weight}}$	Compare Factors: Berthelot 3962
0.5	0.139	0.255	1.535	1.280	3989	+27
0.5	0.139	0.255	1.516	1.261	3929	—33
0.5	0.139	0.255	1.518	1.261	3929	—33
0.6	0.167	0.283	1.783	1.500	3895	—67
0.6	0.167	0.283	1.798	1.515	3935	—27
0.6	0.167	0.283	1.801	1.518	3943	—19
				Average	3937	—25

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It is interesting to compare these results with the nine authorities quoted by Fries[1]. In that list the factors for sugar range between 3866 by Stohman and 4173 by Rechenberg with an extreme variation of 6.42. per cent.

It is not possible here to touch upon other experiments in this line which already indicate equally interesting features along the lines above indicated.

Heat Value of $KClO_3$.—In studying the heat value of potassium chlorate, it is manifestly different from a simple decomposition. The heat value in passing from $KClO_3$ to $KCl + O_3$ would be 105.6 — 95.8, or 9.8 calories per g. molecule, which calculated to the water equivalent of the instrument would call for a correction of 0.023° per one-half g.

Mention has already been made of the fact that, as used in fusion with carbonaceous material, no oxygen pressure is evident upon opening the bomb. This suggests either the use of the oxygen in reaction with the carbon, or the uniting of the same with the oxides of sodium. Probably both combinations occur. In studying the behavior of the chlorate, it was found that by increasing the quantity used, with a constant amount (1/2 g.) of pure carbon, no pressure of free oxygen could be detected until approximately two g. of chlorate had been employed. This suggests the following equations expressing the possible reactions:

$$KClO_3 + 3Na_2O_2 + 3C = KCl + 3Na_2CO_3.$$

Under the conditions indicated by this equation, we might expect to find no free oxygen liberated. Beyond this ratio of chlorate to carbon, however, we would expect to note a pressure of gas, and this conforms to our experience. That is in the ratio of 122.5: 36 or 1.7 g. of chlorate to 0.5 g. of carbon, no pressure is in evidence, but a slight pressure is found when a ratio of two g. of chlorate are used with 0.5 g. of carbon. This fact seems to prove further that part of the oxygen from the chlorate combines with the carbon and part with the Na_2O. It is this latter combination which adds to the heat value of the chlorate above its heat of simple decomposition. If we take such an equation as the following for the probable reaction and calculate the heat due the chlorate under this hypothesis, we shall have

$$KClO_3 + Na_2O = KCl + Na_2O_2 + O_2.$$

$$\frac{(105. + 119.8) - (95.8 + 100.3)}{122.5} \times 1000 = 235 \text{ cal.}$$

By dividing this number of calories per g. of $KClO_3$ by the water

[1] Investigations in the Use of the Bomb Calorimeter. Bull. No. 94 U. S. Dept. Agr. (1907).

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equivalent of the apparatus (2135), we have 0.108 as the rise in temperature for one g. of chlorate when used in combustions. This factor, therefore, has been used in the preceding tables where one g. was the quantity employed.

Whether the oxygen unaccounted for unites directly with carbon or is dissolved in the fusion, or unites to form intermediate or different oxides as suggested by De Forcrand,[1] cannot be affirmed. One further point is to be noted: In use of one g. and also one and one-half g. of chlorate the correction per half g. as above indicated is 0.054°. Of this 0.023° are considered to be the theoretical heat of dissociation of the potassium chlorate. The excess of 0.031° is considered as resulting from some recombination of the liberated oxygen. This reaches its normal height at one g. of chlorate. With less of chlorate this extra heat diminishes. If this extra heat is represented by a rise of 0.031° for one g. and .000° for no chlorate, it would be 0.016° for one-half g. which added to the normal heat of decomposition (0.023), would equal 0.039° as the correction factor to be used when one-half g. of chlorate is employed in combustions. In the calculations and tables thus far, the factor used has been 0.040°, and this also agrees with the experimental data.

Variables.—From the preceding discussion, it would appear that for materials of definite composition the empirical nature of the process has given place to a more nearly theoretical basis. We have been discussing thus far what may be properly termed the constants involved. Coal is not a substance of uniform composition, and it is upon fuels that the use of the method mainly centers. It is in this connection, therefore, that we would expect to find the variables.

Nitrogen.—Probably the most troublesome constituent to correct for in the Mahler type of calorimeter is the nitrogen. In the instrument under discussion, this element does not enter into the case, because in contrast to combustions with compressed oxygen there is no appreciable oxidation of nitrogen where sodium peroxide is the oxidizing medium.[2]

Sulphur.—First on the list of real variables is sulphur. It is now comparatively simple to adopt standard conditions, as for example. by using benzoic acid and potassium chlorate, we can add to such a charge a given weight of the substance to be examined. This has been done with powdered sulphur and also with iron pyrites. Since the conditions with sulphur alone are not widely different from those attending the combustion of iron pyrites, and since it is in the latter form that the sulphur of coal mainly occurs, we will give attention only to this material.

The average of a number of combustions using ¼ g. of carefully

[1] Compt. rend., 128, 1519.
[2] Z. angew. Chem., 17, 1454.

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selected iron pyrites gave an increase in temperature of 0.362°. The relation this reading bears to a correct value is derived as follows:—If we apply the same constants for calculating sulphur as for carbon or hydrogen, the rise in temperature per ½ g, of sulphur would be $\frac{2250}{3117}$ or 0.7225°. The 0.362° rise, found as above indicated, would represent for the corresponding ½ g. of contained sulphur in pyritic form $\frac{0.362}{0.1333 \times 2}$ or 1.356°. From this it appears that the indicated rise per 0.5 g. of sulphur content is too high by 1.356°—0.7225° or 0.634°, and for 0.005 g. of sulphur which would be the equivalent of one per cent. in the usual ½ g. taken, the error would be 0.00634°. It appears from this, therefore, that sulphur, while a variable, can be easily corrected for, by subtracting from the indicated rise in temperature, 0.006° for each per cent. of sulphur in the sample. This is a matter of considerable importance in coals with four or five per cent. of sulphur.

Ash.—The effect of silicious matter in fusion with sodium peroxide should be taken account of, and its determination has been made possible by the same development of standard conditions for testing. The following tests were made: Sample (a) was shale, free from carbonaceous matter, taken immediately above a coal seam; (b) nearly pure amorphous silica which had been previously ignited; (c) finely pulverized glass; (d) a composite ash; (e) dark red ash, high in iron; (f) and (g) were gray ashes low in iron. The last four samples were obtained by burning off a quantity of coal as in the usual ash determination. One-half g. was taken for each test and run in duplicate with the standard charge of 0.5 g. of benzoic acid and 0.5 g. of potassium chlorate. The results are given in Table 9.

TABLE 9.

FUSION OF SILICIOUS MATERIAL WITH SODIUM PEROXIDE.

Substance	Total Rise; (standard + ½ g. silicious matter)	Rise for standard ½ g. Benzoic acid, ½ g. $KClO_3$)	Rise in degrees centigrade for equivalent of 1% ash *i.e.* 0.005 grams
(a) Kaolin	2.288	2.180	0.0011
(b) Shale.	2.320	2.180	0.0014
	2.336	2.180	0.0015
(c) Silica	2.357	2.180	0.0017
	2.359	2.180	0.0018
(d) Glass	2.275	2.180	0.0009
(e) Composite Ash from Ill. coals	2.279	2.180	0.0010
(f) Ash from Sangamon Co., Ill. coals	2.278	2.180	0.0010
(g) Ash from Vermilion Co., Ill. coals	2.297	2.180	0.0012
(h) Ash from Williamson Co., Ill., coals	2.279	2.180	0.0010

From this it appears that a very fair uniformity exists with regard to

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the heating effect of silicious material and a correction of 0.001° is indicated for each per cent. of ash content in the material to be tested.

One other variable is met with, and this is the oxygen compounds or hydroxyl constituents which in coal are sufficiently definite in the different types to make a correction easily applicable. In anthracites and semi-anthracites, of course, there is nothing of this element, at least not in sufficient amount to be taken account of. It is even a question whether it should be corrected for in semi-bituminous coals. In bituminous coals and lignites, however, it should enter into the final correction. The amount of the correction is readily arrived at as follows. We have already observed in connection with benzoic acid and sugar that the hydroxyl constituents when referred to the percentage basis of the water formed in their decomposition, represent a heat value as shown in a rise of temperature equal to 0.0033° for the equivalent of one per cent. of water so combined. In bituminous coals this constituent varies so slightly from 10 per cent. in amount that the corresponding correction of 0.033° is practically a constant component of the correction called for in coals of the bituminous type. In lignites a similar condition exists in that black lignites have a content of this material sufficient to require a correction of 0.056° for each ½ g. used and brown lignites require a correction of 0.111 per ½ g.

Ignition wire.—The value of the fine wire used for ignition by the electric method was determined by fusing a number of wires with a coal of known value as shown in the table.

TABLE 10.

FUSION OF IRON WIRE WITH SODIUM PEROXIDE AND STANDARD COAL.

Weight of iron wire burned	Total Rise	Correction for standard material used	Rise for wire	Rise for 1. gram iron
0.2951	2.840	2.591	0.249	0.844
0.3100	2.856	2.591	0.265	0.855
0.4860	2.990	2.591	0.399	0.821

The wire used in these tests had an average weight of 0.010 g. per 10 centimeters. As the wire was practically all consumed, the correction factor indicated was 0.008° for each length of 10 mm. used.

If we list, therefore, the component parts of the correction factors that enter into the various types of coal, we would have for average conditions the following:

(a) CORRECTION COMPONENTS FOR AVERAGE ANTHRACITE COAL, USING 10 GRAMS Na_2O_2 AND ½ GRAM $KClO_3$.

½ gram $KClO_3$	0.040°
1 per cent. Sulphur	0.006
7 " " Ash	0.007
Fuse Wire	0.008
Total	0.061° C.
or,	0.110° F.

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(b) AVERAGE SEMI-BITUMINOUS COAL (NOT OVER 25 % VOLATILE MATTER.)

½ gram $KClO_3$	0.040°
1 per cent. Sulphur	0.006
7 " " Ash	0.007
4 " " Hydroxyl	0.013
Fuse Wire	0.008
Total	0.074° C.
or,	0.123° F.

(c) AVERAGE BITUMINOUS COAL (OVER 25 % VOLATILE MATTER).

½ gram $KClO_3$	0.040°
2 per cent. Sulphur	0.012
10 " " Ash	0.010
10 " " Combined Water	0.033
Fuse Wire	0.008
	0.103° C.
	0.185° F.

Where the component parts vary widely from these average conditions the ultimate correction factor may readily be made up from the schedule of units as listed under No. 6 of the Summary, below.

Summary.

1. The heat of combustion of carbon is 73 per cent. of the heat of the reaction of the carbon with sodium peroxide.

2. The heat of combustion of hydrogen (to liquid water) is 73 per cent. of the heat of the reaction of hydrogen with sodium peroxide.

3. The sodium peroxide used must be free from absorbed moisture or the correction value of the same must be determined.

4. Standard conditions based upon theoretical data are available for checking material and apparatus.

5. The constants are the large elements in the case and practically govern the accuracy of the process.

6. The correction components may be readily reduced to a unit basis; thus,—

Sulphur	0.006°	for 1% in 0.5 g. of material
Ash	0.001°	" " " " " " "
Combined Water	0.0033°	" " " " " " "
$KClO_3$	0.040°	" 0.5 g. used
Fuse Wire	0.008°	" 10 mg. burned

UNIVERSITY OF ILLINOIS, URBANA.

THE ANALYSIS OF ICE CREAM.

BY CHARLES D. HOWARD.

Received September 5, 1907.

With the recent enactment of standards for ice cream by several of the states, the analysis of this substance is just beginning to receive attention on the part of food inspection chemists. As the literature seems to contain no specific methods, the following (in part simple modifications of

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general methods) are offered as having been in successful use at this laboratory.

Fat.—It is especially desirable to make this estimation as soon as possible after the sample has melted, as it not infrequently occurs that on short standing, even before appreciable souring has taken place, the butter-fat tends to separate in such a manner, and on mixing, returns to the surface so rapidly as to render the removal of a representative portion exceedingly difficult, while if care is not exercised in attempts at emulsifying, butter-clots are apt to be formed.

Except for purposes of approximation, or unless the sample is very largely diluted, the use of the plain Babcock method is not admissible. Leach's copper sulphate method for the estimation of fat in condensed milk is not directly applicable, because of the fact that in this case the fat is not carried down by the precipitated proteids, but persists in rising to the surface, and no other precipitant seems capable of affording any different result.

The procedure finally adopted consists of a modification of Leach's method, involving solution of the fat in chloroform, with the subsequent removal of the latter in a current of steam. Using a blunt-pointed pipette, eighteen grams of the sample are weighed into a Babcock cream bottle, preferably of the Bartlett, or bulb type graduated to 25 per cent. in fifths. Add 3 cc. chloroform and water to about three-fourths the capacity of the bottle. Agitate, add about 10 cc. of Fehling's copper sulphate solution, mix and centrifuge for three minutes, when all of the fat will be found in the underlying chloroform layer. In the presence of appreciable quantities of gum tragacanth or gelatin, the supernatant liquid will persist in remaining turbid; this difficulty may be obviated by the addition of two or three cc. of N/10 alkali, the resulting copper hydroxide serving to precipitate the gum very perfectly. Insert a glass tube of small bore, connect with an aspirator and remove most of the supernatant liquid. Repeat the washing once, then introduce a tube of small bore connected with a source of steam provided with a safety cock, and blow in live steam for two or three minutes, or until the chloroform has been completely expelled; the latter condition is essential. The use of a water bath for the removal of the chloroform is not feasible, as the precipitated proteids retain the latter with great persistency, and its removal is not complete even after prolonged heating in this manner. Cool the contents of the bottle, add water to a volume of 17.5 cc., and proceed as usual, being careful to secure complete solution in the acid of the somewhat hardened proteid substance.

A second method for fat, recommended by the Chicago Board of Health,[1] has been given only a brief trial in this laboratory. This method has

[1] Rep. State Food Commissioner, Illinois, 1906, 80.

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the advantage of rapidity, and is said by those who have used it extensively to give good results. It would seem, however, that some little skill is required in its execution to avoid contamination of the fat column by casein on the one hand, and charring on the other. The procedure is as follows: "Run 9 g. of ice cream into the test bottle. Add 30 cc. of a mixture of equal parts by volume of conc. HCl and 80 per cent. acetic acid. Heat on a water-bath till well darkened, but short of charring. Whirl in a Babcock centrifuge and read the percentage of fat directly. If the cream is charred, ether may be added after whirling. The layer containing the fat is drawn off into another bottle and the ether evaporated. The bottle is then filled with water and again whirled and the fat read directly."

Character of the Fatty Matter.—While the practice is apparently not a common one, there seems to be evidence that in certain sections at least, not a little "ice cream" is put upon the market, the fat of which consists in part or wholly of oleo or cotton-seed oil. For purposes of examination the fatty matter may be advantageously separated by removing 30-40 cc. of the cream layer to a fat-bottle, adding one cc. of strong mercuric nitrate solution and 20 cc. of petroleum ether and whirling in a centrifuge. The ethereal layer is removed, washed with water and the ether evaporated.

Chemical Preservatives.—The presence of borax may be detected by removing five cc. of the separated serum to a porcelain dish, rendering distinctly acid with ten per cent. hydrochloric acid, adding five drops of turmeric tincture and evaporating. For formaldehyde the hydrochloric acid test may be used as a preliminary, but as ice cream free from this body affords by this treatment a purplish brown color, the distillation method should be employed to confirm any positive indication noted. Saccharin and other bodies of this class are detected in connection with the test for gelatin.

Fillers and "Mechanical Preservatives."—The old-fashioned recipes for cheap ice cream call for corn-starch or eggs, the first being quickly detectable and the second indicated by the deep yellow color imparted by the yolks to the underlying serum separating from the sample on standing. At present there is a large number of patent, or secret preparations on the market, most of which consist essentially of gelatin or gum tragacanth. The writer has recently had his attention directed to two such, sold to manufacturers of ice cream under the names of "foamaline" and "cream-puff."

The use of compounds of this description is not altogether for the purpose of taking the place of butter-fat, since manufacturers of high grade cream allege that their addition in small quantity is necessary, in the case of goods intended to be shipped or to be kept over much more than twenty-

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four hours, for the purpose of causing the ice cream to "stand up," that is, retain its homogeneity and obviate the tendency to marginal icing that occurs with storage. It appears that manufacturers are thus able to "hold over" goods under refrigeration for several days or even indefinite periods, in order to await favorable weather or market conditions.

Another substance that is being used to some extent as a filler of ice cream is commercial caesin. Such use in New Hampshire has been observed in several instances—the solidified, cheesy appearance of the caseinous stratum separating from the sample, affording an indication that was later confirmed outside the laboratory. Obviously, a method for detecting this class of goods might be based upon the determination of the increased albuminoid content.

For the detection of gelatin the method of Stokes may be followed, using 10–15 cc. of the mixed sample. Any faint cloudiness corresponding to less than 0.10 per cent. of gelatin is ignored. The main portion of the filtrate from the proteids is then extracted with chloroform and examined for saccharin and similar substances in the usual manner.

Where any considerable quantity of gum tragacanth or a similar substance has been used, such fact is determinable without difficulty. The writer has observed samples of melted ice cream that were fairly stiff from the presence of excessive amounts of gum. However, in those cases where the latter is used for its mechanical effect the quantity may be less than 0.5 per cent., or even as little as 0.25 per cent. In view of the remarkable similarity in the general behavior to reagents of casein and the vegetable gums, and the tendency of the latter to be carried down with the former under the influence of metallic precipitants, the development of a method for the detection of such a small quantity of this class of substances offers more difficulty than might be supposed.

The conversion of the gummy material into mucic acid might be used as a test, but it is of course necessary to first remove all lactose, and the subsequent procedure not only consumes some time, but the results are apt to be rather uncertain, especially in the presence of but 0.2–0.3 per cent. of gum. Reichl and Breinl's orcinol test (Allen, "Commercial Organic Analysis," Volume 1, page 422) would seem to be valuable in this connection, as it affords a striking reaction as applied to the alcohol-washed mixture of gum and casein; unfortunately, however, casein alone appears to give a similar reaction.

A preliminary test that serves well consists in precipitating 10 cc. of the separated serum with acetone, washing with two or three portions of dilute alcohol (using a centrifuge). The washed residue is boiled with 6–8 cc. of water, and 1 cc. sodium hydroxide (1–10) for about thirty seconds. This treatment results in the formation of albuminates largely soluble in hot alcohol. The gum is converted into pectates soluble in

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water, but insoluble in hot alcohol, while any gelatin is decomposed into bodies not precipitable by alcohol. The liquid is cooled and allowed to stand a few minutes to facilitate the separation of any insoluble caseinous matter; filtered, filtrate heated to boiling, one and one-half volumes of warm alcohol added and mixed. In the presence of 0.2 per cent. of gum tragacanth or agar-agar, a characteristic flocculent precipitate will *immediately* separate. Any turbidity, or slight precipitation on standing a few moments, should be ignored. The precipitated pectate may be dissolved in cold water and the solution saturated with ammonium sulphate for the purpose of demonstrating the absence of any appreciable quantity of proteids.

A second procedure, involving more or less complete preliminary removal of proteids and bases, with conversion of the gum into pectic acids, consists in boiling 10 cc. of the separated serum to 5 cc. after addition of one half cc. of concentrated hydrochloric acid. Two volumes of alcohol are then added to the hot liquid and the resulting precipitate washed two or three times with alcohol. The residue is boiled with 5 cc. of water and one drop of strong acetic acid and filtered hot. The resulting filtrate is rendered just neutral or very faintly alkaline, boiled and filtered. Finally 1 cc. of sodium hydroxide (1–10) is added to the filtrate, the latter boiled for a few seconds, followed by the addition of one and one-half volumes of alcohol, noting any precipitation of alkaline pectate.

NEW HAMPSHIRE LABORATORY OF HYGIENE.

THE DETECTION AND DETERMINATION OF BENZOIC ACID IN KETCHUPS, FRUITS AND CIDERS.

BY HARRY S. REED.

Received Sept. 6, 1907.

The following methods were worked out by the writer on occasion of being called upon to determine the presence of, and quantity of benzoic acid, in certain fruits, ketchups, ciders, etc. They are presented in the hope that some one may find them useful.

Detection of Benzoic Acid.—For this purpose a modification of Mohler's test is used. One hundred g. of the substance under examination is acidified with dilute sulphuric acid and thoroughly and repeatedly extracted with chloroform. The chloroform extract is separated from the water solution each time as far as possible by means of a separatory funnel. The last traces are then spun out with a centrifuge. The success of both qualitative and quantitative determinations depends largely on the care with which the extraction is made.

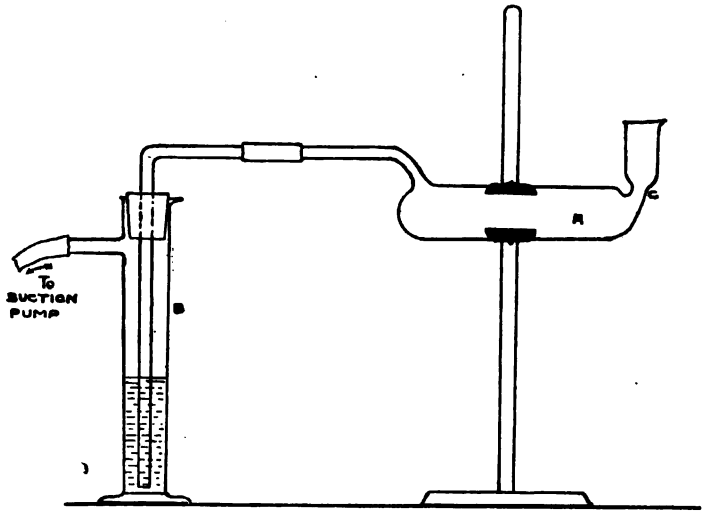
The chloroform extract is then placed in the reservoir (A) of the following apparatus:

(Capacity of A., 50 cc.)

(Capacity of B., half filled, 12 cc.)

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(A) is detached, connected directly with a suction pump, and the chloroform allowed to evaporate spontaneously under a current of air. After the evaporation is completed, (A) is placed in a desiccator. When



perfectly dry it is again attached to (B) and completely submerged to the neck of the funnel (c) in a sand bath. The suction is now connected to (B), which contains approximately normal sodium hydroxide and the temperature of the sand raised slowly to 145°. It is kept at this temperature for a few minutes, and finally brought up to 260°. The benzoic acid is thus sublimed and then retained in (B) as sodium benzoate.

The water solution of sodium benzoate is next removed from (B), placed in a separatory funnel, acidified with dilute sulphuric acid, and extracted with chloroform. This chloroform solution of benzoic acid is now placed in a porcelain evaporating dish, and made alkaline with alcoholic potassium hydroxide. The residue obtained by evaporating the chloroform and alcohol from the above solution on a water bath is tested for benzoic acid by the same reactions utilized in Mohler's test, the procedure, however, is slightly different.

In the first place no water is added, as it was found that in case only a very small quantity of benzoic acid was present, it would be lost when the concentrated sulphuric was added to the water solution of benzoic acid. So the residue of potassium benzoate is decomposed directly by concentrated sulphuric acid and heated over an open flame until white fumes appear. The sulpho-benzoic acid now formed is oxidized to *m*-dinitrobenzoic acid and the organic matter oxidized by use of potassium nitrate. Very little will be necessary since if the extraction has been

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carefully done, there will be very little organic matter to be disposed of. The acid solution of *m*-dinitrobenzoic acid is now cooled, diluted with water, cooled again, made alkaline with ammonium hydroxide and reduced with hydrogen sulphide. The reduction is accomplished by passing the gas through the solution in the same evaporating dish with which the test was started, necessitating no transference of the solution, and the least tint of cherry red color caused by the reduced product, the ammonium salt of *m*-diaminobenzoic acid, is readily discernible against the white background of the evaporating dish.

The Determination.—Quantitatively the method employed for the determination of benzoic acid is based on two conditions. The first, that chloroform very completely extracts benzoic from many other vegetable acids, as malic, tartaric, oxalic, etc., in water solution; and the second, that the calcium salt of benzoic acid is far more soluble in cold water than the calcium salts of the other acids mentioned.

The process consists in following the same method of extraction which is used in the qualitative test. Take the chloroform extract obtained from the water solution of sodium benzoate contained in (B) of the above apparatus, and allow this to evaporate spontaneously in a beaker. Add to this residue 25 cc. of milk of lime containing 0.0145 g. metallic calcium to each cubic centimeter. This milk of lime is prepared by acting on water with metallic calcium. Then 25 cc. of the milk of lime are poured into another beaker, and is to be subjected to the same treatment as the former. This serves as a blank. Returning to the beaker containing the extract, after the addition of the milk of lime its contents are evaporated to dryness on a water bath. The acids present in the extract are converted into calcium salts and the excess of calcium hydroxide largely into calcium carbonate. This residue is now taken up with 25 cc. of water, filtered and washed with 15 cc. of water. Care must be taken to use exactly the same quantities of water on the blank. The filtrate is allowed to run into a platinum evaporating dish, in which it is evaporated to dryness on a water bath. The residue should contain only calcium salts of benzoic and carbonic acids. These are now ignited over a blast lamp and burned to calcium oxide. The calcium oxide is dissolved with 2 cc. of twice normal hydrochloric acid and titrated back with normal tenth sodium hydroxide using phenolphthalein as an indicator. The amount of calcium present in the blank is subtracted from that found present in the test and the difference calculated to benzoic acid.

The chief objection to the above methods lies in the fact that it requires considerable time to carry them out successfully. I have no doubt, however, as to their exactness. The quantity of benzoic acid in cranberries gives excellent results. By drying the substance under exami-

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nation very slowly at a low temperature, I have detected as little as forty-four hundred thousandths of one per cent. I give below the results of my last determination of benzoic acid in tomato ketchup.

Two samples were taken and to one, 0.12 g. of sodium benzoate (0.1 g. benzoic acid) was added. Original sample, sodium benzoate, found equals 0.0531 per cent. ; benzoic acid equals 0.045 per cent.

Original sample plus added sodium benzoate, sodium benzoate, found = 0.172 per cent. ; benzoic acid = 0.145 per cent.

Subtracting :—

0.172 — .12 (added) = 0.052 sodium benzoate.
0.145 — .1 " = 0.045 benzoic acid.

CHEMICAL DEPARTMENT,
MICHIGAN AGRICULTURAL COLLEGE.

SOLUBILITIES AND EXTRACTION VALUES OF FOOD COLORS.

BY EDWARD GUDEMAN.
Received June 28, 1907.

Few data are found in the literature on the solubilities and the extractive values of the vegetable and coal tar colors commonly used in foods. In collaborating with the Association of Official Agriculture Chemists, the following report was submitted to Prof. E. F. Ladd, Associate Referee on Colors. It was recommended by the Referee that special attention be given among other points, to investigations along the following lines :—

a—Solubility of coal tar and vegetable dyes, in various solvents, ether, acetic ether, petroleum ether, methyl and ethyl alcohols, acetones, etc., and mixtures thereof, arranging the compounds according to their solubility as—easily soluble, difficultly soluble and insoluble.

b—Extractive values of the various solvents for dyes in neutral, acid and alkaline solutions.

The terms "easily soluble", and "difficulty soluble" being very indefinite, the actual amounts of color dissolved and extracted were determined.

In determining the solubility of the colors, certain factors must be taken into consideration and considered as constants, *viz* : Amount of color to solvent ; time of bringing into solution, and temperatures.

In determining the extractive values, the constants must be : Amount of color in solution ; amount of solvent to solution extracted ; time of extraction and temperatures.

Working with colored food products, naturally colored or otherwise, the extraction values will be materially affected by the unknown factors, due to the composition of the food products, the presence of oils, fats, saccharine substances, nitrogenous matter, fiber, mineral substances (ash), etc., which may change the extractive properties of many solvents, and which in many cases act as mordants on the colors themselves, so that

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the data obtained on the colors themselves will not be conclusive and often of little or no value. In working on food products directly, it has been found advantageous to separate the colors by means of dyeing tests[1] modifying the tests, when necessary, so as to extract without addition of any salts or mordants, and dyeing large pieces of wool (6x24 inches) in hydrochloric acid, ammonia and neutral baths. The extraction value of the color fixed on the wool can then be determined directly on part, and other tests applied to the rest of the cloth. The color is separated from a part of the dyed cloth and a second dyeing test made with this, thereby separating many of the natural colors and enabling the investigator in some cases to identify by chemical and solubility tests, the actual class or kind of color present in the food product.

The results obtained on the solubilities and extractive values as applied to colors in or separated from food products is left for a later report, the investigation not having been concluded.

In determining the solubility—cold—all reagents were at room temperature (18°–20°). One gram of the color was thoroughly shaken for one minute with 100 cc. of the solvent. The solution was allowed to stand for one hour. If not perfectly clear, it was clarified either by filtration or in a centrifuge. The actual amount of color dissolved was determined by direct comparison, in color tubes, using known standard solution of the same color for comparison. No attempt was made to completely dissolve or extract any colors, by continued treatment.

In determining the solubility—hot—the solutions were immersed in a boiling water bath for 30 minutes, shaken every five minutes, flasks being connected with reflux condensers. The hot solutions were filtered quickly, using a suction pump when necessary. The filtrates were compared with standard solutions of the same color. It was found that an increase in time of heating or varying the amount of the solvent, slightly changed the amount of colors dissolved, in many cases. This was especially noticeable with colors that gave some soluble part differing in shade or color from the original color. Impurities in the colors themselves, due to raw materials used or processes of manufacture, may be extracted by some solvents and thereby give slight color to the solvent, not actually due to the color itself. The extraction of colors by means of solvents, is a method of partial or complete purification of food colors. The tables of solubilities show that only small differences exist between hot and cold solutions, although in some cases the solvent became supersaturated and allowed some of the color to separate or crystallize out on cooling.

All solvents used were redistilled and dried with calcium chloride for

[1] Sostegni and Carpentieri, Arata, Bull., 65, Bureau of Chemistry, Dept. of Agr.

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solvent tests; for extraction tests the drying was omitted. When the solubility of the color is less than one to 2000, the results are not conclusive, as this may be due to the moisture contained in the color itself and taken up by the solvent. In some cases, with very low solubility it was found that on drying with calcium chloride, after treatment, the color disappeared from the solvent and colored the calcium chloride. As many of these colors are sensitive to heat, no attempt was made to dry the colors themselves, the amount of moisture present varying from 0.5 to 6.0 per cent., depending on the class of color and kind of package in which it was kept. The absolutely dry color will absorb moisture quickly unless kept in hermetically sealed packages.

Many of the colors are very sensitive to acids and alkalies, reacting so quickly that they can be used as indicators, and many of them are used for that purpose. The shade of the color is often changed due to the solvent being either acid or alkaline in character.

The extractive values were determined by dissolving one g. of color in 1000 cc. of distilled water for the neutral solutions, in 1000 cc. of hydrochloric acid, containing one per cent. by weight of the acid for the acid solutions and in 1000 cc. of dilute ammonia water, containing one per cent. of ammonia by weight for the alkaline solutions.

100 cc. of the different solutions, containing 0.1 g. of color, were thoroughly shaken with 50 cc. of the solvent, allowed to stand until a clear distinct separation had taken place. The amount of color extracted was determined by comparison with the standard color solutions of same character, acid, alkaline or neutral. If the solvent was not clear, it was filtered and with colors forming emulsions, the separation was made in a centrifuge. No attempt was made to obtain complete extraction. Very low extractive values are also not conclusive, as the small amount of color going into the solvent may be due to water extracted by the solvent, it also was found, that drying the solvent with calcium chloride would take out the color in the same manner as with the solubility tests. All extractions were made cold, at room temperature. The following colors were partially or completely examined:

Coal tar colors:

Amberine Yellow, Amethine Violet, Saffoline Red, Ruby Red, Amaranth Red, Rasberine Red, Turquine Blue, Turmerinc Yellow, Myrtiline Green, Marsiline Orange, Oroline Yellow, Carminoline, Hoffman Violet Ponceau 2 R, Fuchsine S.B., Indigo Carmine A, Naphthol Yellow, Orange R, and Bismark Brown.

Vegetable colors:

Primoline Yellow, Citronole Yellow, Cochineal, Cochineal Rose, Samoline Orange, Celoline Blue, Chestnut Brown, Koncentrona L, Pansoline

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Violet, Veroline Green, Aecoline Yellow, Lazuline Blue, Mintoline Green, Cladonal Red, Turmeric, Annatto and Chlorophyll.

The most commonly used colors in the confectionery industry are the

TABLE I

SOLUBILITIES OF DRY COLORS.

Color = 1.0000 g.

Solvent = 100 cc.

Grams of Color Dissolved per 100 cc. Solvent.

Name of Colors Kind of Color	Oroline Yellow Coal Tar		Amaranth Red Coal Tar		Turquine Blue Coal Tar		Aecoline Yellow Vegetable		Cladonal Red Vegetable		Lazuline Blue Vegetable	
	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot
Water	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Hydrochloric Acid 1%	1.0000[1]	1.0000[1]	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Ammonia 1%	1.0000	1.0000	1.0000	1.0000	Color Destroyed		1.9000	0.9000	1.000[2]	1.000[2]	1.0000	1.0000
Ethyl Alcohol	0.1500	0.8000	0.0300	0.0300	0.0700	0.1000	0.0100	0.1000	0.0010	0.0100	1.0100	1.0200
Methyl Alcohol	0.2500	1.0000	0.0500	0.0500	0.1000	0.2000	0.0150	0.0150	0.0020	0.0050	0.0400	0.0800
Amyl Alcohol	0.0400	0.0400	0.0200	0.0200	0.0010	0.0010	0.0100	0.0100	0.0005	0.0005	0.0020	0.0020
Petroleum Ether	0.0030	0.0030	Yellow		0.0000	0.0000	0.0020	0.0020	0.0000	0.0000	0.0000	0.0000
Ether	0.0080	0.0080	Yellow		0.0000	0.0000	0.0050	0.0050	0.0000	0.0000	0.0000	0.0000
Acetone	0.0080	0.0150	0.0050	0.0050	0.0000	0.0000	0.0050	0.0050	0.0000	0.0000	0.0010	0.0010
Ethyl Acetate	0.0100	0.0250	0.0005	0.0005	0.0010	0.0010	0.0020	0.0020	0.0050	0.0050	0.0005	0.0005
Amyl Acetate	0.0100	0.0100	Yellow		0.0000	0.0000	0.0050	0.0050	0.0005	0.0005	0.0005	0.0005
Carbon Disulphide	0.0030	0.0030	0.0010	0.0010	0.0000	0.0000	0.0010	0.0010	0.0002	0.0002	0.0010	0.0010
Carbon Tetrachloride	0.0020	0.0020	0.0010	0.0010	0.0000	0.0000	0.0005	0.0005	0.0002	0.0002	0.0005	0.0020
Chloroform	0.0020	0.0020	0.0020	0.0030	0.0000	0.0000	0.0015	0.0015	0.0001	0.0002	0.0005	0.0020

[1] Color changed to red.

[2] Color changed to blue.

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TABLE 2.

EXTRACTION VALUES OF COLORS.

Solutions = 1.0000 g. Color to 1000 cc.

Solvents = 500 cc. per Extraction

Grams of Color Extracted by 500 cc. Solvent.

Name of Color / Kind of Color	Oroline Yellow Coal Tar			Amaranth Red Coal Tar			Turquine Blue Coal Tar			Aecoline Yellow Vegetable			Cladonal Red Vegetable			Lazuline Blue Vegetable		
Solution	Neutral	Acid 1 %	Alkali 1 %	Neutral	Acid 1 %	Alkali 1 %	Neutral	Acid 1 %	Alkali 1 %	Neutral	Acid 1 %	Alkali 1 %	Neutral	Acid 1 %	Alkali 1 %	Neutral	Acid 1 %	Alkali 1 %
Solvents Used																		
Water							...			Slightly Cloudy								
Hydrochloric Acid 1%	Changes to Red									Clear, lighter shade								
Ammonia 1%				Changed to Orange			Color Destroyed			Clear, deeper shade			Changed to blue					
Ethyl Alcohol	Miscible			Miscible			Miscible			Miscible			Miscible			Miscible		
Methyl Alcohol	Miscible			Miscible			Miscible			Miscible			Miscible			Miscible		
Amyl Alcohol	.010	.5000	.0000	[1]	.600	[1]	.0010	.5000	.0[2]	.0500	.3500	.0000	.0050	.7000	.0005	.0010	.3000	.0100
Petroleum Ether	.001	.0010	.0020	0.	.000	[1]	.0000	.0000	.0[2]	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
Ether	.005	.0080	.0040	0.	.000	[1]	.0000	.0000	.0[2]	.0080	.0500	.0000	Yellow	Yellow	.0000	.0000	.0000	.0000
Acetone	Miscible			Miscible			Miscible			Miscible			Miscible			Miscible		
Ethyl Acetate	.015	.0150	.0005	[1]	[1]	[1]	.0005	.0005	.0005[3]	.0500	.6500	.0500	.0020	.0050	.0010[4]	.0000	.0000	.0005
Amyl Acetate	.002	.0050	.0150	0.	[1]	.0000	.0000	.0000	.0[2]	.0050	.0200	.0000	.0010	.0050	.0005	.0000	.0000	.0000
Carbon Disulphide	.000	.0000	.0000	0.	.0000	.0000	.0000	.0000	.0[2]	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
Carbon Tetrachloride	.000	.0000	.0000	0.	.0000	.0000	.0000	.0000	.0[2]	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
Chloroform	.000	.0000	.0000	0.	.0000	.0000	.0000	.0000	.0[2]	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000

[1] Color extracted yellow.

[2] Color destroyed by alkali, reproduced by acid.

[3] Color extracted is blue.

[4] Color extracted is blue.

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reds, blues and yellows. Most other colors are mixtures and combinations of these three colors. The foregoing tables give the results obtained on three vegetable colors and three coal tar colors, having similar shades and having exceptional great color intensities for the classes of colors they represent.

Examination of these tables shows that the use of miscible solvents like methyl and ethyl alcohols and acetone are of no value for extraction purposes. Solvents of an acid like character (ethyl acetate) are not suitable as the results obtained are misleading, due to the effect of the solvent on the color.

The solubilities of many colors in petroleum ether, ether, carbon disulphide, carbon tetrachloride and chloroform is so slight, that these solvents are very suitable for preliminary extraction of food products thereby extracting oils and fats, before making dyeing tests to separate the colors. Care must be exercised, as many colors are soluble in fats or oils and are liable to be extracted in such preliminary treatment. Examination of the fats or oils will show whether any color has been extracted with these.

Conclusions drawn from a very large number of solubility and extraction tests, extending over a long period of time, are that the colors extracted or dissolved by many solvents under varying conditions from neutral, acid or alkaline solutions, give no conclusive data for deciding upon the character or class of the colors themselves. The differences in solubility and in extractive values of vegetable colors compared with coal tar colors, are no greater, nor less, than the differences found between the various colors themselves, belonging to the same class of colors.

Comparative color intensities were also determined and it was found that only a very limited number of vegetable colors, had a color intensity equal to one-fourth that of a corresponding shade of coal tar color and that the largest number of vegetable colors had one-tenth or less color intensity, than the corresponding coal tar color of similar shade.

The colors used were supplied to me by Messrs. H. Kohnstamm & Co., to whom I wish to express my thanks for assistance rendered.

903 POSTAL TEL. BLDG., CHICAGO.

[FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY OF THE DEPARTMENT OF MEDICINE OF THE UNIVERSITY OF PENNSYLVANIA.]

ON THE DIGESTION OF URINE IN THE DETERMINATION OF NITROGEN BY THE KJELDAHL METHOD.

BY P. B. HAWK.

Received September 15, 1907.

Having made use, in several metabolism experiments, of various modi-

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fications of the Kjeldahl method for the determination of nitrogen, I concluded that it would be of interest to determine whether, under the same conditions, there was any reason for preferring any particular one of these modifications used by me, in different laboratories, with satisfactory results, in the determination of the nitrogen content of the urine. Each of the modifications had been carefully checked at the time of using, but obviously, of course, I had never made simultaneous determinations of nitrogen upon the same sample of urine by means of each of the modifications. It was also desired, in this connection, to secure data regarding the rapidity of digestion under various conditions. The modifications of the Kjeldahl method which have been used by me in the determination of nitrogen in the urine, are those which entail the following procedures as to preliminary digestion of the specimen:

Method I.—Five cubic centimeters of urine were treated with 20 cc. of concentrated sulphuric acid in a Kjeldahl digestion-distillation flask, 0.2 g. of powdered cupric sulphate added and the mixture boiled until the digestion was complete. From the data which are summarized on the following page it will be seen that this process of digestion was completed in *thirty minutes*, provided care was taken to see that the Bunsen burners were in proper condition to produce the maximum amount of heat. The usual method of distillation was employed.

Method II.—Exactly the same as the first method, given above, except that 0.2, 0.5 or 0.7 g. of mercury was used in the digestion instead of 0.2 g. of cupric sulphate. This procedure was accompanied, of course, by the use of potassium sulphide in connection with the concentrated alkali in the final distillation.

Method III.—Exactly the same as the second method, given above, except that 5 g. of potassium sulphate were added to the digestion mixture after the sulphuric acid had reached the boiling-point and the flask had been cooled somewhat.

Experimental Data.

In every instance, 20 cc. of concentrated sulphuric acid and 5 cc. of the same urine sample were used in the digestion. The final distillations were always conducted under like conditions as to *length of the distillation period* and *volume of the distillate*. Special attention was given the Bunsen burners of the digestion apparatus in order to secure the maximum amount of heat. The results of the tests are given in tabular form below:

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Determination of Total Nitrogen in a 24-hour Sample of Urine, 20 cc. of Concentrated Sulphuric Acid Used in Each Case. The Results Give the Number of Grams of Nitrogen in 1200 cc. of Urine.

	0.2 gram		0.4 gram		1 gram	
	Digested 30 minutes	Digested 90 minutes	Digested 30 minutes	Digested 90 minutes	Digested 30 minutes	Digested 90 minutes
Powdered $CuSO_4$	14.33	14.34	14.25	14.29	13.82	13.79
	14.28	14.36	14.22	14.21	13.75	13.87
	14.35	14.37			13.92	13.83
	14.33	14.31			13.80	
		14.28				
$CuSO_4$ solution	14.34	14.30	14.28	14.27		
	14.31	14.35	14.31	14.25		

	0.2 gram		0.5 gram		0.7 gram	
	Digested 30 minutes	Digested 90 minutes	Digested 30 minutes	Digested 90 minutes	Digested 30 minutes	Digested 90 minutes
Potassium sulphate (5 grams) and mercury	14.31	14.30	14.30	14.35	14.32	14.35
	14.22	14.33	14.35	14.26	14.30	14.29
		14.27	14.35	14.32	14.27	
		14.31	14.21			
		...	14.27			
Mercury	14.27	14.20	14.24	14.30	14.26	14.24
	14.29	14.23				
		14.25				

NOTE.—Tests made with a digestion period of 20 minutes, gave in every instance, much lower results than those tabulated above.

Conclusions.

1. Method I, as outlined above, is as satisfactory as any of those tried, for the digestion procedure in the determination of nitrogen in the urine. This method entails the use of 0.2 g. of powdered cupric sulphate in the digestion process. It is no more accurate than methods II and III as outlined, but it is preferred because of the fact that the method includes the use of fewer reagents and therefore allows of the saving of considerable time, particularly where large numbers of determinations are made, as is frequently the case in extensive metabolism studies.

2. In the case of urine, the digestion is complete in thirty minutes, when either of the methods, as outlined, is used. However, when time permits, it is advisable to continue the digestion for a somewhat longer period.

3. The presence of an excess of cupric sulphate in the digestion mixture occasions a loss of nitrogen, the data showing a somewhat higher percentage of nitrogen when 0.2 g. of cupric sulphate was used, than that obtained when the amount of cupric sulphate was raised to one gram.

4. Cupric sulphate may be used to equal advantage in powdered form or in solution, the only point to be borne in mind in this connection

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being that the most satisfactory amount to add, whether in powder or in solution, is 0.2 g.

5. Urine cannot be satisfactorily digested, by any of the means mentioned in this article, in less than thirty minutes.

NEW BOOKS.

PRACTICAL TEST-BOOK OF CHEMISTRY. BY JOHN DABNEY PALMER., M.A., M.D. New York: John Wiley & Sons. Price $1.00.

This handy little volume of 190 pages will be useful to pharmacists and practising physicians. While the book does not by any means contain enough material to justify the claim made in the preface of serving as a "*safe guide for testing any substance presented for examination*" it will, nevertheless, be helpful to the analytical chemist in cases where the substance under examination happens to be treated by the author. The book is made up of two parts: Specific Tests and Tests for Purity. The first part contains identification reactions for many of the most important alkaloids, glucosides, bitter principles and synthetic remedies together with a few inorganic substances, like alum and ammonia. The second part contains directions for detecting adulterations in some definite compounds, like alcohol, chloroform, etc., as also in many other substances used either as foods, medicines or in the arts. A list of principal reagents employed is given in the book along with their methods of preparation. The book is supplied with an exhaustive table of contents and an alphabetical index which is very incomplete. The choice of material is not very evident. Many rare substances are included while substances of frequent occurrence are left out. Alcohol and chloroform are treated, but ether and benzene are not mentioned. Tests for butter, sausage, triptopine and several other rare alkaloids are given, but cheese, lemon oil and other important substances are left out. Borax and alum receive notice, but nothing is said about washing soda, potassium iodide or bromide. The specific tests are, as a rule, quite simple and easily carried out; in fact, the author purposely avoids complicated operations or special apparatus. Neither the polariscope nor the refractometer are used in the indentification tests. Even the separatory funnel is replaced by a simple glass tumbler. The wisdom of such simplifications may well be questioned. The tests for some substances are quite exhaustive, while for others the tests are so meagre that even melting points are not stated. The directions given as specific tests will usually be found sufficient for the identification of pure substances, but those under the name of tests for purity will in many cases show only adulterations of the crudest kind. Phenacetin is treated in two different places, on pages 7 and 98, giving two sets of specific tests but no melting point is given in either place.

H. M. GORDIN.

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MERCK'S 1907 INDEX. THIRD EDITION. An encyclopedia for the chemist, pharmacist and physician, stating the names and synonyms, chemical nature and formulas, physical form, appearance and properties, melting and boiling points, specific gravities and methods of testing, physiological effects, therapeutic uses, modes of administration and application, ordinary and maximum doses, incompatibilities, antidotes, special cautions, hints on keeping and handling, etc., of the chemicals and drugs used in chemistry, medicine and the arts. Merck & Co., New York.

The chief difference between this and the previous editions consists in the introduction of a large number of crude drugs and the omission of exact price quotations. The approximate price of any chemical listed in the Index can be easily found by a system of numbers as explained in the preface. The large amount of useful information in a very concise form should make the book very valuable to chemists, physicians and pharmacists. H. M. GORDIN.

SIX LECTURES ON THE THERMODYNAMIC POTENTIAL AND ITS APPLICATION TO PROBLEMS OF CHEMICAL AND PHYSICAL EQUILIBRIUM, INTRODUCED BY TWO LECTURES ON CONCENTRATED SOLUTIONS AND OSMOTIC PRESSURE. BY J. J. VAN LAAR. Braunschweig, F. Vieweg & Son, 1906. Price 3.50 marks.

If one should enter a staid house of worship and without previous warning find in the pulpit the Reverend Bill Sunday exhorting the congregation with coatless harangue, he might experience the same surprise and shock as comes to the traveler in the austere realm of thermodynamics when he first peruses this little book of van Laar's. From the cold page of print we probably get little idea of the fervor with which these lectures were originally delivered. But what the printer could do he has done. The exclamation point is the favorite mark of punctuation, and the print becomes more emphatic with the growing intensity of the author, until in the peroration it culminates in a type of such size and blackness as a yellow journalist might view with pride.

In the first chapter the author discusses the dangers that first arise when the laws of dilute solutions are applied to concentrated solutions. With special severity he deals with the hydrate numbers which Jones has calculated, by first assuming that the freezing-point lowering of every solution really follows the law of van't Hoff, and then finding the degree of hydration which would account for any observed discrepancy. "In this way", says the author, "we can prove anything." The force of this criticism is, however, to some extent lost when in the second chapter the author himself makes a calculation in which unconsciously, he uses a method of reasoning which is identical in principle with that of Jones, and somewhat less justifiable. He assumes that the physical behavior of any simple liquid can be calculated from that of any other simple liquid. The fact that this is not true of most liquids, he ascribes to association, and from the discrepancy between the calculated behavior and that observed, he calculates the degree of association. Thus he states

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as an incontrovertible fact that water at 0° contains 80 per cent. of double molecules.

The third chapter consists of a passionate onslaught upon osmotic pressure. The author considers that this conception has rendered important service to science, but believes that its usefulness is over, and shows how it may be replaced by the thermodynamic potential. In this war on what he calls the "dilute school" of chemists he recognizes the services of his ally Jahn. After quoting liberally from the latter, he writes, "All this is so plainly and correctly expressed that I, in my struggle of twelve years, have hardly expounded it better." – – – "Now we can say that time has justified me completely. Osmotic pressure runs on its last legs, and the thermo-dynamic potential gains influence everywhere."

The remaining six chapters are devoted to an elementary exposition of the thermo-dynamic potential and its application to special physico-chemical problems. Here the author to a great extent abandons the fierce polemic style of the previous chapters, and his elementary statement and proof of the fundamental thermodynamic equations are remarkably clear and effective. In the later chapters, however, where van der Waals' theory of liquids is introduced, it is sometimes difficult for the reader to distinguish between pure thermodynamic equations and those which possess only approximate or hypothetical validity.

Throughout the book the style is vivacious and interesting, and the reviewer usually concurs heartily in the opinions expressed. He regrets therefore that the author's extreme partizanship makes it impossible to recommend the volume to those who are not already somewhat familiar with the principles of thermodynamics. GILBERT N. LEWIS.

TENTH ANNUAL CONVENTION OF THE ASSOCIATION OF STATE AND NATIONAL FOOD AND DAIRY DEPARTMENTS, HELD AT HARTFORD, CONNECTICUT, JULY 17-20, 1906. 8vo., vi + 349 pp. John Wiley & Sons, New York, 1907. Cloth $3.00.

This association is to be congratulated on having its proceedings appear in a manner commensurate with its dignity, in a continuous and readable form, instead of being interspersed with advertising matter as in past years.

Even to a greater degree than in previous years, the 1906 convention was characterized by a most notable series of able papers by the leading food experts in the country. In addition to the usual reports of committees and miscellaneous addresses, the following papers were presented and recorded in full in the proceedings, together with interesting discussions in many cases:

"Conflict of Laws", by George L. Flanders; "Food Work in Foreign Countries", by A. L. Winton; "A Few Thoughts for the Good of the Order", by T. K. Bruner; "City Milk Inspection", by J. Q. Emery; "Cheese Making in the Colorado Climate", by Mary Wright; "Color and

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Antiseptics in Butter", by E. K. Slater; "The Value of Household Tests in Detecting Food Adulteration", by J. Hortvet; "The Food Law and the Experts", by H. W. Wiley; "Food from the Consumer's Point of View", by Alice Lakey; "Pure Food Work in Indiana", by H. E. Barnard; "Canned Goods and their Adulteration", by E. F. Ladd; "The Pure Food Issue—Some of its Problems", by R. M. Allen; "American Milk and Milk Standards", by Wm. Frear; "Harmony of Standards", by Richard Fischer; "Extracts and Beverages", by O. S. Marckworth; "The Use of Sulphurous Acid in Food Products" by C. D. Howard; "Port Inspection", by R. E. Doolittle; "From the Canner's Standpoint Concerning Further Legislation", by J. T. Olney; "The Normal Constituents of Whiskey", by J. H. Shepard.

These papers and discussions cover a wide range of live topics, treated almost without exception by specialists in close touch either with the practical enforcement of the food laws from the standpoint of the food commissioner, or with the composition of food and detection of adulteration from the analyst's point of view.

The book is gotten out in attractive form and will be found indispensable to the ever increasing corps of workers and students in food control work.

In a useful appendix are given regulations of the U. S. Department of Agriculture governing the inspection, labeling and transportation (interstate and foreign) of meat and meat products, together with the rules and regulations for the enforcement of the Food and Drugs Act of June 30, 1906, the text of the Act itself, and some of the important food inspection decisions of the Agricultural Department. ALBERT E. LEACH.

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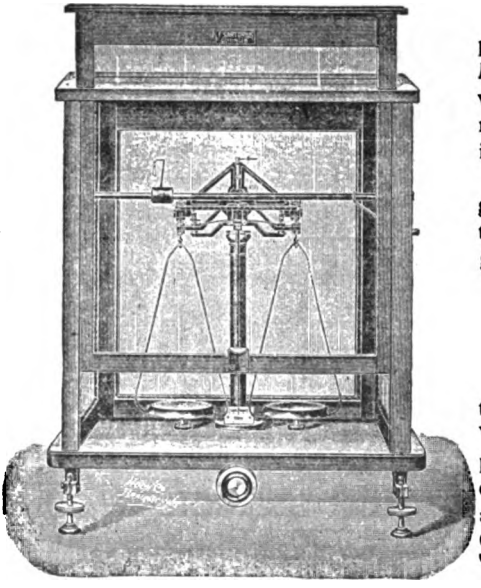
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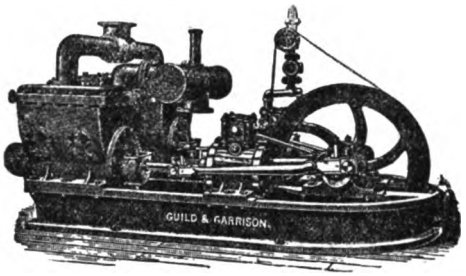
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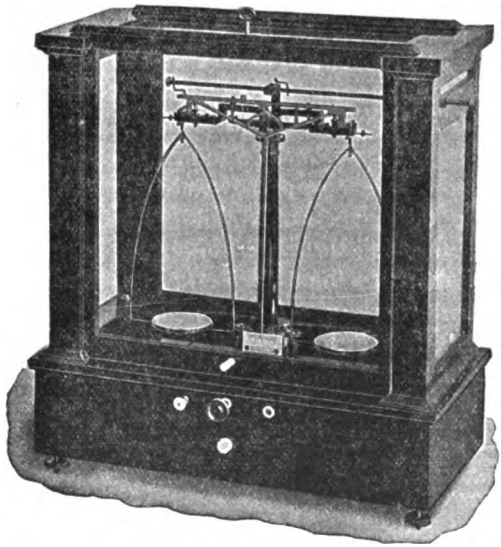
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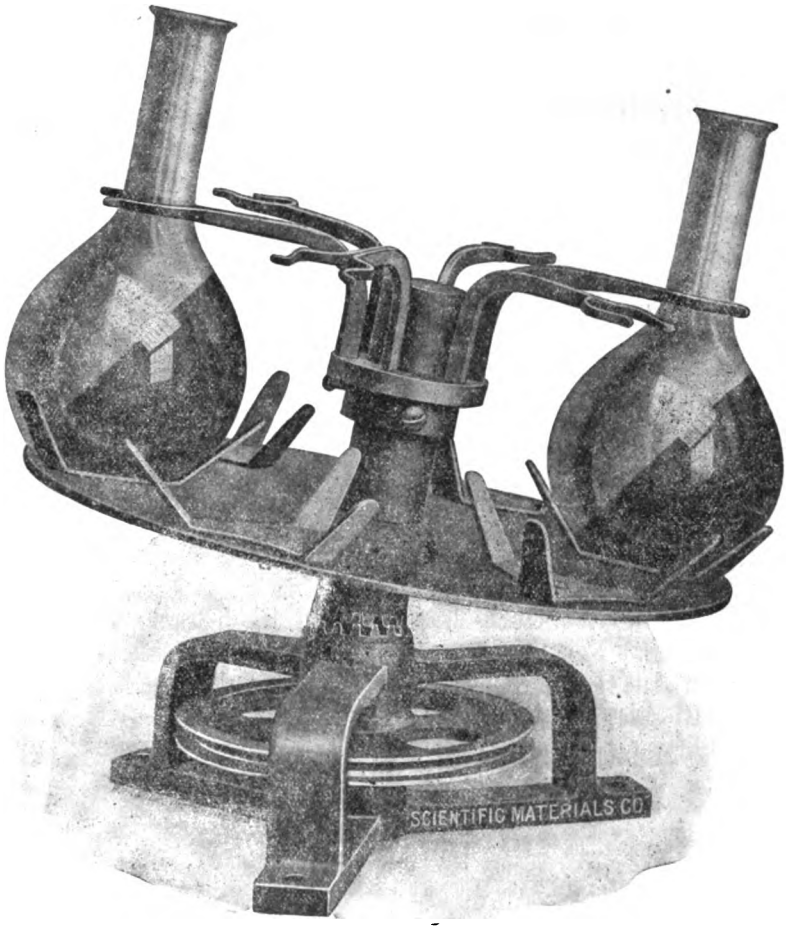
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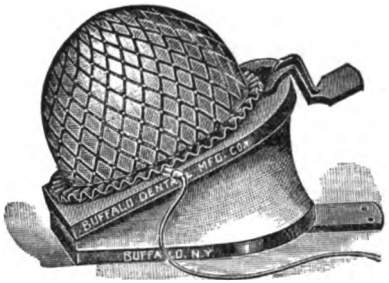
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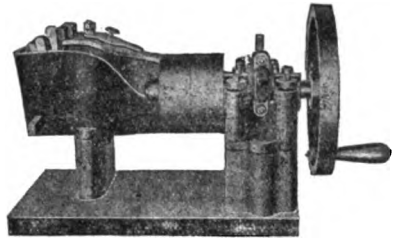
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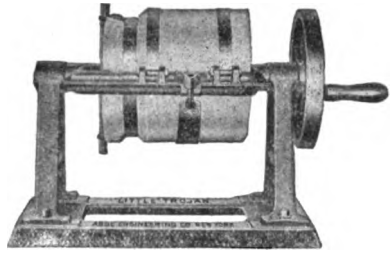


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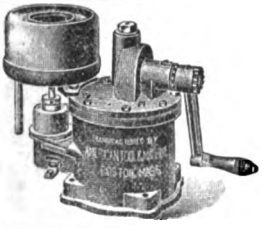
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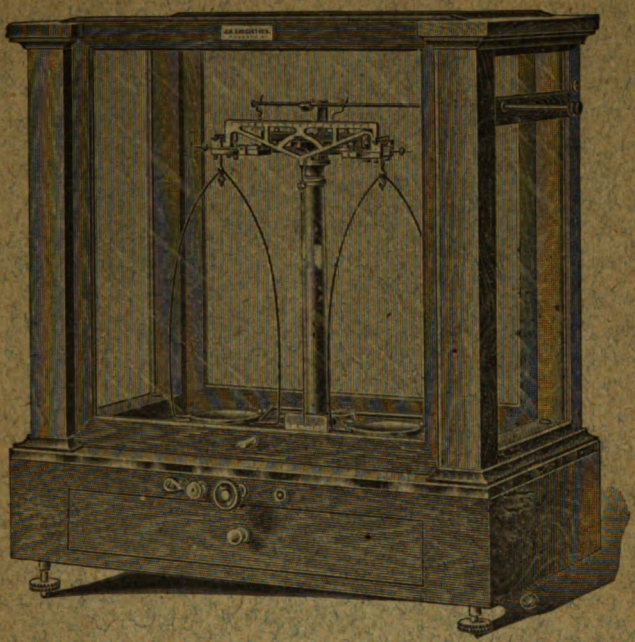
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THE EQUILIBRIUM RELATIONS OF CHROMATES IN SOLUTION.

BY MILES S. SHERRILL.
From experiments by F. M. Eaton, Alden Merrill and D. E. Russ.
Received September 23, 1907.

Introduction.

The constitution of chromates in aqueous solution has been the subject of a number of investigations. Walden[1] measured the conductance of solutions of normal chromates, of dichromates and of chromic acid. According to his measurements, solutions of chromic acid, CrO_3, and of hydrochloric acid at the same molal concentration have approximately the same conductance; moreover the equivalent conductance of chromic acid, also like that of the strong monobasic acids, varies but little with the concentration. These facts indicate that chromic acid exists in solution either as H_2CrO_4 dissociating thus,

$$H_2CrO_4 = \overset{+}{H} + H\overset{-}{C}rO_4,$$

or, as Ostwald[2] has pointed out, as $H_2Cr_2O_7$ dissociating without the formation of any very large amount of an intermediate HCr_2O_7-ion directly into H-ion and Cr_2O_7-ion according to the reaction,

$$H_2Cr_2O_7 = 2\overset{+}{H} + \overset{=}{C}r_2O_7.$$

To test the correctness of this latter conception Ostwald determined the freezing-point of a solution containing 0.5-mol of CrO_3 per liter. The lowering of the freezing-point due to one mol of dichromic acid, $H_2Cr_2O_7$, for complete dissociation according to the second reaction, would be three times that produced by one mol of an undissociated substance. This factor, known as the van't Hoff factor, on the other hand, would be equal to four, for complete dissociation of the same amount of acid according to the first reaction. The value found experimentally by Ostwald was somewhat less than three, and after correcting for dissociation of the

[1] Z. physik. Chem., 2, 49 (1888).
[2] Ibid., 2, 78 (1888).

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acid by means of the conductivity data of Walden, corresponded very closely to the existence of dichromic acid in solution.

This view of the constitution of chromic acid in solution has been very generally accepted by other investigators, and the possible existence of any appreciable amount of an $HCrO_4$ -ion entirely overlooked.[1] If this is not neglected, both of the above reactions must be considered in determining how chromic acid exists in solution. The relative amounts of $HCrO_4$ -ion and Cr_2O_7 -ion present will depend on the concentration and on the value of the equilibrium constant of the reaction,

$$2H\overline{C}rO_4 = H_2O + \overline{C}r_2O_7.$$

The same equilibrium equations must hold also in chromate and dichromate solutions. Thus potassium chromate in aqueous solutions shows an alkaline reaction due to the following hydrolysis,

$$\overline{C}rO_4 + H_2O = H\overline{C}rO_4 + \overline{O}H.$$

This hydrolysis goes on to a greater extent than it ordinarily would because the hydrochromate ion is removed from the solution by the above dehydration to form the dichromate ion.

On the other hand dichromates show an acid reaction because the dichromate ion becomes hydrated to a certain extent to form the hydrochromate ion, which in turn is slightly dissociated into the hydrogen ion and the chromate ion.

It was the purpose of this investigation to test the above conception of the equilibrium relations of chromates in solution, and to determine if possible, the values of the equilibrium constants involved. The work was started by F. M. Eaton in February, 1905, carried on further by A. Merrill in 1906, and completed by D. E. Russ in May, 1907. Their results will be presented in the order in which the experiments were carried out.

The Freezing-Point of Dilute Solutions of Chromic Acid and of Potassium Dichromate.

Experiments by F. Malcolm Eaton.

As already shown, a determination of the lowering of the freezing-point produced by chromic acid or by dichromates offers one means of studying their constitution in solution. Such measurements heretofore have always been made in rather strong solutions. If as above assumed, the dichromate ion becomes hydrated to form the hydrochromate ion, the conditions most favorable for its formation would be in the more dilute solutions, according to the mass-action law. Accordingly freezing-point determinations of dilute solutions of these two substances were made.

[1] In an article which appeared in the *Z.* anorg. Chem., 54, 265 (1907) since the completion of this investigation, Spitalsky does take this into consideration. His paper is discussed in the latter part of this article.

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Before beginning these determinations the question arose as to whether the hydration of the dichromate might not be a time reaction, and hence the results obtained be dependent on the time taken to form the experiment. To answer this question the solubility method used by Hudson[1] in his work on the hydration of milk sugar was employed. When a salt in solution undergoes hydration the final equilibrium between the anhydrous salt and the solution will be reached only when the hydrated part is in equilibrium with the anhydrous part, which in turn is in equilibrium with the solid salt. If the hydration takes an inappreciable time, equilibrium will be reached quickly. If on the other hand hydration takes place slowly, the experimentally found solubility will vary with the time taken and with the way in which equilibrium is approached.

The following solubility experiments were made with potassium dichromate. Three excess portions of powdered salt were kept for thirty minutes in contact with water at 100°, 30°, and 20° respectively, then bottled separately and rotated in the thermostat at 20°. In this way equilibrium was being approached in the first two cases from supersaturation, and in the last case from undersaturation. From time to time 10 ccm. samples were pipetted off and analyzed by titration against ferrous ammonium sulphate. The results are given in Table 1, where the concentrations are expressed in gms. of potassium dichromate in 100 ccm. solution, and the time in minutes from the moment of entering the thermostat.

TABLE 1.

Time	Concentration		
	(1)	(2)	(3)
10	12.47	12.10	11.56
60	11.34	11.43	11.43
240	11.34	11.43	11.52

At the time the samples were first taken, equilibrium had not been reached, but after an hour's interval equilibrium seems to have been established, as no apparent increase is noted even after three hours longer rotation. It is therefore evident that the hydration of the dichromate-ion is complete in a short time.

This conclusion is verified by certain conductivity measurements of Costa[2] on chromic acid solutions. He found, namely, that the conductivity of a chromic acid solution at 0° remained unchanged by heating the solution to a considerably higher temperature and then cooling rapidly to the lower temperature.

The method employed in the determination of the freezing-points was a modification of that described by Richards[3]. The apparatus consisted

[1] This Journal, 26, 9, (1904).

[2] Gazz. chim. ital., 36, I, 535 (1906).

[3] Z. physik. Chem., 44, 563, (1898).

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of a wide-mouthed bottle of about two liters capacity enclosed in a large glass battery jar, the intervening space being firmly packed with felt or cotton. The battery jar was then placed in a pail and the space between the two filled with a mixture of finely crushed ice and water. By these means conduction of heat to or from the inner bottle was reduced to a minimum.

The bottle was further provided with a stopper with three holes, through which extended a tube carrying a plug of glass wool at the lower end to act as a filter, a Beckmann thermometer, and an "up and down" stirrer made of a piece of thick glass rod the lower end of which was flattened and bent horizontally into an arc of about 180°.

In beginning a run with this apparatus the bottle was half filled with a mixture of pure ice (frozen distilled water) ground fine, and distilled water. This mixture contained a large enough proportion of water to allow a thorough mixing by the stirrer. The stopper was now placed in position with the sampling tube, the thermometer, and the stirrer. By stirring at the rate of about one hundred strokes to one minute, and taking readings of the temperature every minute, equilibrium was found to be established in about five minutes so that the next five readings did not vary more than 0.001°. This reading was taken as the freezing-point of the pure solvent.

About 10 ccm. of a strong solution of the substance under investigation was now added and the mixture stirred until readings taken after minute intervals remained constant for five minutes. A pipette was then connected by a rubber connection to the upper end of the sampling tube, and two 10 ccm. portions withdrawn and discarded. Then a sample of the liquid was withdrawn in the same manner, 20 ccm. in the case of the dilute solutions and 10 ccm. in the case of the concentrated, and set aside for subsequent analysis. The mixture was then stirred quickly, the temperature taken, a duplicate sample withdrawn, and the temperature again read. In these temperature readings before and after sampling there was a variation of not more than 0.002°, and the analysis of duplicate samples agreed within one per cent.

A new addition of strong salt solution was now made, enough water being added to make the volume up to the original amount, and the process continued. By previously cooling the water and the solutions added, the amount of ice melted could be made very small and the series extended at small intervals over great ranges.

To ascertain the accuracy of the method two series of determinations of the freezing-points of potassium chloride solutions were made, the concentrations of the samples being determined by conductivity measurements at 25°, and the results compared with those of Hebb[1] in his most accurate work.

[1] Proc. and Trans. Nova Scotia Inst. Sci., 10, 4 (1901).

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The results obtained are shown in Table 2, the corresponding lowerings as taken from Hebb's tables being also given.

TABLE 2.

	Conc.	Obs. low.	Low. from Hebb
Series I	0.0252	0.089°	0.090
	0.0311	0.111	0.111
	0.0391	0.137	0.139
Series II	0.0136	0.048	0.049
	0.0332	0.117	0.116
	0.0453	0.159	0.160
	0.0550	0.194	0.194
	0.0686	0.242	0.241
	0.0900	0.317	0.315

From these results it will be seen that with only ordinary precaution, the readings can be depended on to 0.002°, and with special precautions it is probable that much finer work may be done.

In applying this method to potassium dichromate solutions the concentrations of the samples were determined by titration against standard ferrous ammonium sulphate. Four independent runs were made, the results being shown in Table 3. Concentrations are expressed as mols of potassium dichromate in one liter of solution.

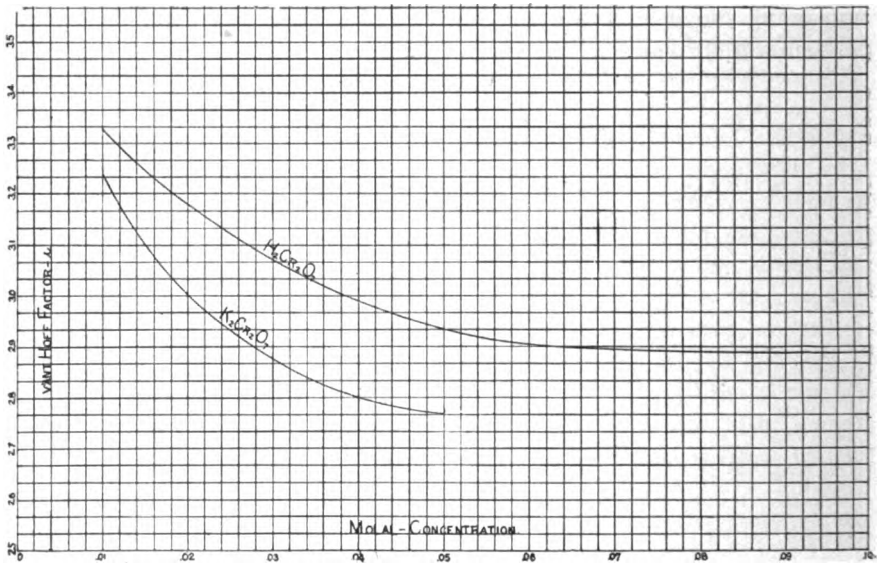
TABLE 3.

Ccm. taken	Conc.	Lowering	i
10	0.01384	0.081°	3.16
10	0.02053	0.113	2.98
10	0.02889	0.154	2.88
10	0.03975	0.202	2.75
10	0.04850	0.244	2.71
10	0.05340	0.263	2.66
10	0.00510	0.035	3.70
10	0.01105	0.067	3.28
10	0.01525	0.090	3.19
10	0.01973	0.112	3.07
10	0.02760	0.150	2.94
10	0.03359	0.178	2.87
20	0.00639	0.038	3.22
20	0.01234	0.070	3.07
10	0.01807	0.098	2.93
10	0.02355	0.127	2.92
10	0.03004	0.158	2.84
10	0.03615	0.183	2.74
20	0.00764	0.047	3.33
20	0.01220	0.072	3.19
10	0.01743	0.098	3.04
10	0.02825	0.150	2.87
10	0.03680	0.190	2.79
10	0.04000	0.203	2.74

In the last column of the table are given values of the van't Hoff factor

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i, that is the ratio of the observed lowering to that which would have been produced had the potassium dichromate remained as $K_2Cr_2O_7$ unionized in solution. It is evident that the maximum value of this factor corresponding to complete dissociation of the dichromate according to the reaction, $K_2Cr_2O_7 = 2\overset{+}{K} + \overset{=}{Cr_2O_7}$, is *3*; while that for complete transformation into hydrochromate and complete dissociation thus, $2KHCrO_4 = 2\overset{+}{K} + 2\overset{-}{HCrO_4}$, is *4*. The variation of *i* with dilution may be best observed by considering the accompanying curve, in which the concentrations are plotted as abscissae and values of *i* as ordinates. The fact that the values obtained in solutions less than 0.02-molal are actually greater than *3*, indicates that not an inappreciable amount of the hydrochromate ion is present in these solutions. That the curve is concave upwards is conclusive evidence that the change of *i* is not simply due to an ordinary increase of dissociation.



A similar line of investigation was carried out with chromic acid. Reasons for considering chromic acid in solution as analogous in constitution to a dichromate have already been mentioned. In Table 4 are shown the results of two independent series of freezing-point determinations. Concentrations are there expressed as mols $H_2Cr_2O_7$ in one liter of solution.

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TABLE 4.

Ccm. taken	Conc.	Lowering	i
20	0.00958	0.059°	3.33
10	0.03340	0.189	3.06
10	0.04690	0.257	2.96
10	0.07180	0.387	2.92
10	0.10160	0.548	2.91
20	0.01370	0.083	3.26
20	0.02730	0.155	3.07
10	0.05880	0.305	2.90
10	9.06440	0.347	2.90
10	0.07670	0.408	2.89

The curve constructed from these data shows a close resemblance to that from the potassium dichromate. That the two are not identical is to be ascribed to a difference in the dissociation relations in the two solutions, and in order to make any quantitative interpretation of the results it is first necessary to make some assumption regarding these dissociation relations.

In the case of the potassium dichromate the solution may be considered as consisting of a mixture of $K_2Cr_2O_7$ and $KHCrO_4$, and hence the following principle shown by Noyes[1] is applicable. This principle states that in a mixture of salts having one ion in common, the degree of ionization of each salt is that which it would have if present alone at such an equivalent concentration that the concentration of either of its ions were equal to the sum of the equivalent concentrations of all the positive or negative ions in the mixture. The sum of the equivalent concentrations of all the positive or negative ions in the mixture may without any great error be considered equal to that ion concentration in a solution containing either salt alone at an equivalent concentration equal to the total equivalent salt concentration in the mixture. To obtain actual values for the degrees of ionization the further principle may be used that salts of the same type have at the same concentration the same degree of ionization.

Accordingly the assumptions as to dissociation relations made in the following considerations were that the ionization of the $K_2Cr_2O_7$ in the solution is the same as that of K_2SO_4, and the ionization of the $KHCrO_4$ like that of KCl at a concentration equal to the total equivalent concentration of salt present. The numerical values for the degrees of ionization were calculated from the conductivity measurements of Archibald[2] made at 0° with potassium sulphate and potassium chloride solutions. The further assumption is made that the ionization of the hydrochromate ion does not take place to an appreciable extent. This is justified by measurements made in another part of this investigation.

[1] Science, 20, 583 (1904); Z. phys. Chem., 52, 635 (1905).

[2] Proc. and Trans. Nova Scotia Inst. Sci., 10, 33 (1898).

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If C represents the total concentration of salt present expressed as atomic in chromium, γ_1 the ionization of the $K_2Cr_2O_7$ in the solution, γ_2 that of the $KHCrO_4$, and i has the significance given in the previous tables, the four following condition equations may be formulated, in which the symbols correspond to molal concentrations.

$$\frac{\overline{\overline{Cr_2O_7}}}{K_2Cr_2O_7} = \frac{\gamma_1}{1-\gamma_1} \qquad (1)$$

$$\frac{\overline{HCrO_4}}{KHCrO_4} = \frac{\gamma_2}{1-\gamma_2} \qquad (2)$$

$$C = \overline{HCrO_4} + 2\overline{\overline{Cr_2O_7}} + 2K_2Cr_2O_7 + KHCrO_4 \qquad (3)$$

$$\frac{C}{2} \times i = 2\overline{HCrO_4} + 3\overline{\overline{Cr_2O_7}} + K_2Cr_2O_7 + KHCrO_4 \qquad (4)$$

In the last equation $\frac{C}{2} \times i$ represents the total molal concentration of the solution as indicated by the freezing-point. Therefore

$$\frac{C}{2} \times i = \overset{+}{K} + \overline{HCrO_4} + \overline{\overline{Cr_2O_7}} + K_2Cr_2O_7 + KHCrO_4$$

This equation can be put in the form of equation (4) by combining with it the additional condition equation,

$$\overset{+}{K} = \overline{HCrO_4} + 2\overline{\overline{Cr_2O_7}}.$$

From the four above equations may be calculated for each case the concentrations of $KHCrO_4$, $K_2Cr_2O_7$, $\overline{HCrO_4}$, and $\overline{\overline{Cr_2O_7}}$ respectively, and hence the equilibrium constant for the reaction, $\overline{\overline{Cr_2O_7}} + H_2O = 2\overline{HCrO_4}$. This constant, $\overline{\overline{Cr_2O_7}}/(\overline{HCrO_4})^2$, will hereafter be designated K_H, and spoken of as the hydration-constant for the dichromate ion.

The results of such calculations are given for a number of concentrations in Table 5. The values of i are taken from the plot, and therefore correspond to a mean of the several determinations.

TABLE 5.

Conc. Total Chromium C	van't Hoff Factor i	Ionization $K_2Cr_2O_7$ γ_1	Ionization $KHCrO_4$ γ_2	Conc. $K_2Cr_2O_7$	Conc. $KHCrO_4$	Conc. $\overline{\overline{Cr_2O_7}}$	Conc. $\overline{HCrO_4}$	$K_H = \frac{\overline{\overline{Cr_2O_7}}}{(\overline{HCrO_4})^2}$
0.02	3.24	0.83	0.943	0.00090	0.00054	0.00438	0.00891	55
0.04	3.00	0.785	0.925	0.00286	0.00101	0.01044	0.01241	68
0.06	2.88	0.755	0.913	0 00529	0.00147	0.01629	0.01539	69
0.08	2.80	0.728	0.905	0.00812	0.00193	0.02172	0.01840	64
0.10	2.77	0.712	0.896	0.01074	0.00266	0.02645	0.02278	51
							(Mean)	61

The dissociation relations in the chromic acid solutions differ from

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those in the potassium dichromate solutions in virtue of the fact that there is a relatively large concentration of hydrogen ion present. This will have the effect of entirely preventing the ionization, $H\bar{C}rO_4 = \overset{+}{H} + \overset{=}{C}rO_4$, which was considered negligibly small in the potassium dichromate, but on the other hand it will render the conditions most favorable for the formation of an $HCr_2O_7^-$-ion. As already pointed out, however, conductivity measurements on chromic acid show that this latter ion does not form to, at least, any great extent. Though the above considerations and the results indicate that it is not strictly correct, yet for want of a better assumption for a quantitative treatment of the results with chromic acid the same assumptions as to ionization relations were made with the chromic acid as were made with potassium dichromate, the $H_2Cr_2O_7$ corresponding to the $K_2Cr_2O_7$, and the H_2CrO_4 to the $KHCrO_4$. The results of the calculations are given in Table 6.

TABLE 6.

Conc. Total Chromium C	van't Hoff Factor i	Ionization $H_2Cr_2O_7$ γ_1	Ionization H_2CrO_4 γ_2	Conc. $H_2Cr_2O_7$	Conc. H_2CrO_4	Conc. $\overline{\overline{Cr_2O_7}}$	Conc. $\bar{H}CrO_4$	$K_H = \frac{\overline{\overline{Cr_2O_7}}}{(\bar{H}CrO_4)^2}$
0.02	3.33	0.830	0.943	0.00079	0.00062	0.00377	0.01029	36
0.04	3.18	0.785	0.925	0.00225	0.00143	0.00823	0.01762	26
0.06	3.07	0.755	0.913	0.00423	0.00223	0.01302	0.02330	24
0.07	3.03	0.740	0.908	0.00537	0.00264	0.01529	0.02603	23
							(Mean)	27

Considering the rather arbitrary assumptions made in these calculations the agreement of the values of the hydration-constant among themselves in the separate cases of the potassium dichromate and chromic acid solutions, and also of the mean values obtained from them is as good as could be expected. The calculation is very sensitive with respect to the ionizations assumed, and also with respect to the i value. For example, if in Table 5 at the concentration 0.02-normal, the ionizations assumed had been *0.82* and *0.93* instead of *0.83* and *0.94* respectively, the calculated value of K_H would have been 47 instead of 55. The effect of changing i from *3.24* to *3.33* may be seen by comparing the values obtained for the constant at this concentration in the dichromate and chromic acid solutions respectively. The calculated value changes from *55* to *36*.

This method of evaluation of the hydration-constant for the dichromate ion can be considered, therefore, as giving only the right order of magnitude. The results do indicate conclusively, however, the existence of the hydrochromate ion in no inappreciable amount.

It was thought that some idea of the amount of hydration could be obtained by measuring the absorption spectra of solutions of chromic acid, potassium dichromate, and potassium chromate. This was done with

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solutions of different concentrations, being careful in each case to have the same amounts of salts present in the two solutions in question, but varying the amount of water in which the salt was dissolved.

The results showed that potassium dichromate and chromic acid give identical absorption bands, cutting out all light beyond the bright green. No change was noticed on dilution, although the amount of water was increased ten-fold. A solution of potassium chromate gave practically no absorption in any part of the spectrum except the violet and extreme blue. It is therefore evident that the acid is very similar to the dichromate as pointed out by Ostwald[1], and that the hydrochromate ion is not very different in color from the dichromate ion.

The Hydrolysis of Ammonium Chromate by Means of Electrical Conductivity.

Experiments by Alden Merrill.

The hydrolysis of ammonium chromate may be represented by the reaction,

$$\overset{+}{N}H_4 + \overset{=}{C}rO_4 + H_2O = H\overset{-}{C}rO_4 + NH_4OH.$$

The subsequent formation of any dichromate in these experiments is considered as negligibly small.

If ammonia be added to a solution of ammonium chromate, the hydrolysis, according to the mass action law, must be driven back, thus increasing the concentration of the NH_4-ion in the solution, and converting the $HCrO_4$-ion to the doubly charged CrO_4-ion. This change would have the effect of increasing the conductivity of the solution by an amount which is a measure of the extent to which the salt had been hydrolyzed.

The exact relation between the change of conductance and the fraction hydrolyzed is shown by the following considerations.

The equivalent conductance Λ_1 of an ammonium chromate solution at a given equivalent concentration C, assuming no hydrolysis to have taken place, is given by the expression

$$\Lambda_1 = \gamma\Lambda_{NH_4} + \gamma\Lambda_{CrO_4}, \qquad (1).$$

where γ is the ionization of the ammonium chromate at the concentration in question. If the salt now be considered as hydrolyzed by the fractional amount h, then the solution will contain $(NH_4)_2CrO_4$, NH_4HCrO_4, and NH_4OH, at the equivalent concentration $(1-h)C$, $\frac{h}{2}C$, and $\frac{h}{2}C$ respectively. If further, γ_1 equal the ionization of $(NH_4)_2CrO_4$ and γ_2 that of the NH_4HCrO_4 in the mixture, and the conductance of the NH_4OH be neglected, then the expression for the equivalent conductance Λ_2 of the ammonium chromate becomes

[1] Loc. cit.

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$$\Lambda_2 = \gamma_1(1-h)\Lambda_{NH_4} + \gamma_1(1-h)\Lambda_{CrO_4} + \gamma_2\frac{h}{2}\Lambda_{NH_4} + \gamma_2\frac{h}{2}\Lambda_{HCrO_4} \qquad (2).$$

The ionization γ_1 of ammonium chromate in the mixture will not differ essentially from γ, the ionization of ammonium chromate assuming no hydrolysis. Furthermore the unionized fraction $(1-\gamma_1)$ of the ammonium chromate in the mixture may be estimated as twice the unionized fraction $(1-\gamma_2)$ of the ammonium hydrochromate.[1] That is

$$\gamma_1 = \gamma, \text{ and } (1-\gamma_1) = 2(1-\gamma_2)$$

Placing γ_1 and γ_2 in equation (2) in terms of γ with the help of these equations, and subtracting the resulting equation from equation (1) the following expression is obtained for the change of conductance $\Delta\Lambda$ produced by the hydrolysis.

$$\Delta\Lambda = \gamma h\Lambda_{NH_4} + \gamma h\Lambda_{CrO_4} - \frac{1+\gamma}{4} h\Lambda_{NH_4} - \frac{1-\gamma}{4} h\Lambda_{HCrO_4}.$$

This solved for h gives

$$h = \frac{4\Delta\Lambda}{\gamma(3\Lambda_{NH_4} + 4\Lambda_{CrO_4} - \Lambda_{HCrO_4}) - (\Lambda_{NH_4} + \Lambda_{HCrO_4})} \qquad (3).$$

The change in the equivalent conductances $\Delta\Lambda$ may be measured, as above indicated, by measuring the increase in the equivalent conductance of ammonium chromate produced by adding enough ammonia to completely drive back the hydrolysis. The conductance of the added ammonia may, of course, be corrected for. To calculate the hydrolysis from such a measurement it is evidently necessary to know all of the terms occurring in the denominator of the above equation. The equivalent conductance Λ_{NH_4} of the ammonium ion is given by Kohlrausch, that, Λ_{CrO_4}, of the chromate ion, as well as the value of γ, may be computed, as shown later, from the conductivity measurements made with ammonium chromate. In order to determine the equivalent conductance Λ_{HCrO_4} of the hydrochromate ion, the conductance of solutions of potassium dichromate and of chromic acid were measured at varying concentrations.

For these experiments, stock standard solutions of ammonium hydroxide, potassium dichromate and chromic acid were prepared, from which were made up the solutions whose conductance was to be measured.

The ammonia used was obtained from Baker and Adamson, and was marked strictly C. P., free from amines, carbonate and silicate, sp. gr. 0.90. Its conductance compared well with the values given by Kohlrausch. The solution was analyzed by direct titration against standard hydrochloric acid, methyl orange being used as the indicator. The stock solution was kept in a two-liter bottle fitted with a rubber stopper carry-

[1] See Noyes: Science 20, 584 (1904).

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ing glass tubes as in a wash bottle. One tube served as a siphon for filling a 30 ccm. side arm burette, the other was connected with a series of potash bulbs to remove any carbon dioxide from the air, thus preventing any formation of ammonium carbonate.

The potassium dichromate was purified by repeated crystallizations from water, and was dried to constant weight at 110°. The stock solutions were prepared by dissolving a weighed amount of salt in water and diluting to the required volume by means of a graduated flask, conductivity water being used.

The chromic acid was purified by repeated crystallizations from water till free from sulphates. The stock solution was analyzed by standardizing against iron wire by the usual volumetric method. The value of this iron wire in terms of chromate was first determined by titration with a standard potassium dichromate solution. By this means any impurity of the iron wire, or inaccuracy in obtaining the absolute end point was eliminated. As the neutral ammonium chromate solutions later used were prepared by mixing exactly equivalent amounts of chromic acid and ammonium hydroxide, a very careful analysis was necessary. As a check on the above analysis the stock solution was also analyzed gravimetrically as follows. An excess of lead acetate was added to the solution, and the precipitate of lead chromate filtered through a Gooch crucible, washed thoroughly, and ignited to constant weight. The Gooch crucible during the ignition was supported in an asbestos ring inside of a large porcelain crucible, the latter being subjected to the full heat of a Tirrell burner. The two methods of analysis gave practically identical results.

All conductance measurements in this work were made in a thermostat kept constant at 18° within $\pm 0.03°$. At the time of measurement the exact temperature was noted and a corresponding correction of 2 per cent. per degree was applied. The specific conductance of the water used for the various dilutions varied from 1 to 2×10^{-6}. In each measurement a corresponding correction was made. The method used was the ordinary one of Kohlrausch, the slide wire and rheostat used being carefully calibrated.

For the measurements with potassium dichromate the usual form of Arrhenius cell with platinized electrodes quite close together was in general used. For one or two measurements, however, at the higher concentrations the pipette form of cell described below was employed. The cell constant was found by measuring in the cell, the conductance of 0.01 normal solutions of potassium chloride and sodium chloride, and a mean of the values thus obtained was used in the subsequent calculations.

The results of those measurements are given in Table 7.

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TABLE 7.

POTASSIUM DICHROMATE.

Concentration ($\frac{1}{2}K_2Cr_2O_7$)	Specific Conductance κ	Equiv. Conductance Λ
0.04	0.004152	103.3
0.02	0.002132	106.6
0.01	0.001078	107.8
0.005	0.0005465	109.3
0.002	0.0002200	110.0
0.001	0.0001109	110.9

CHROMIC ACID.

Concentration ($\frac{1}{2}H_2Cr_2O_7$)	Specific Conductance κ	Equiv. Conductance Λ
0.02	0.006900	345
0.01	0.003482	348
0.0025	0.000875	350
0.001	0.000349	349
0.0005	0.0001742	348.4

The values given of the specific conductance are the mean of several readings with different resistances and with different fillings of the cell.

It is to be noted that in the case of the dichromate the increase in the equivalent conductance with the dilution is abnormally small even considering the chromate as a salt of the type of potassium chloride. This effect may be explained by the fact that on dilution the dichromate ion becomes hydrated to form the slower moving hydrochromate ion. Ionization of the latter would tend to have the opposite effect, that is to give an abnormally large increase in the conductance with the dilution. Some measurements of Whetham[1] on the conductance of potassium dichromate in very dilute solution are in accordance with this, and will be discussed more in detail later. On account of these complications no attempt was made to compute a value for the equivalent conductance for the hydrochromate ion from the measurements.

With the chromic acid solutions the case is somewhat better inasmuch as the ionization of the hydrochromate ion is prevented by the presence of the large concentration of the hydrogen ion. Assuming that in the solution 0.0025 atomic in chromium, chromic acid exists entirely as $H_2CrO_4 \rightleftharpoons \overset{+}{H} + H\overset{-}{C}rO_4$ ionized to the same extent as hydrochloric acid at this concentration, the equivalent conductance $\Lambda_{0(H_2CrO_4)}$ at zero concentration for chromic acid may be calculated from the proportion, $\Lambda_{0.0025(HCl)} : \Lambda_{0(HCl)} = \Lambda_{0.0025(H_2CrO_4)} : \Lambda_{0(H_2CrO_4)}$. Using the data of Kohlrausch for hydrochloric acid in the calculation, this value becomes *358*. By deducting from this the equivalent conductance Λ_H for the hydrogen ion *318*, a value is obtained for the equivalent conductance Λ_{HCrO_4} for the hydrochromate ion equal to *40*. For the reasons

[1] Pr. Roy. Soc., 71, 332 (1903).

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above mentioned this can be considered as only an approximation to the true value, but an inspection of the expression given for the hydrolysis of ammonium chromate will show that it will suffice for that calculation.

In the measurements with the ammonium chromate solutions especial precautions had to be taken to prevent any formation of ammonium carbonate from the carbon dioxide of the air. The conductivity cell used was essentially a pipette with platinized vertical electrodes sealed on the inside. The requisite volumes of chromic acid and ammonium hydroxide solutions were drawn from burettes into a graduated glass-stoppered flask which had previously been filled with air-free from carbon dioxide. Dilution to the mark on the flask was made with conductivity water at 18°. By means of a wash bottle arrangement this solution was forced over with a blast of air free of carbon dioxide, into the pipette form of cell. The cell was always first rinsed with several portions of the solution, and finally several measurements made with independent fillings of the cell.

In the solutions to which an excess of ammonium hydroxide had been added it was necessary to make a correction for its conductance. This correction can be computed by making the following substitutions in the mass-action equation for the ionization-constant κ_B, for ammonium hydroxide, and solving for the specific conductance of the ammonium hydroxide. The concentration in equivalents per cubic centimeter of the ammonium ion in the solution is equal to $\kappa_S / \Lambda_{0(S)}$, the ratio of the specific conductance of the salt to its equivalent conductance at zero concentration; similarly that of the hydroxide ion is equal to $\kappa_B / \Lambda_{0(B)}$, the ratio of the specific conductance of the ammonium hydroxide to its equivalent conductance at zero concentration; and finally the concentration C_B of the unionized ammonium hydroxide is equal to that of the added ammonium hydroxide. The expression thus obtained for the specific conductance of the added ammonium hydroxide is

$$\kappa_B = \frac{\kappa_B \times C_B \times \Lambda_{0(B)} \times \Lambda_{0(S)}}{\kappa_S \times 10^6}.$$

The value used in the calculations for κ_B, $\Lambda_{0(B)}$, and $\Lambda_{0(S)}$ were 17.1×10^{-4}, 237.6, and 141.3 (obtained from later measurements) respectively.

In Table 8 are placed all the results of the measurements and calculations. The values of the specific conductance always represents the mean of at least two fillings of the cell. Where duplicate values are given each value corresponds to a complete experiment including the making up of the solution from the stock solutions.

It is evident from the results that the addition of ammonium hydroxide, equivalent in amount to the salt present, is sufficient to completely drive back the hydrolysis. The equivalent conductance obtained in the presence of the added ammonium hydroxide is therefore the equivalent con-

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TABLE 8.

Conc. of added NH_4OH	Spec. conductance of solution	Spec. conductance of NH_4OH κ_B	Equivalent conductance Λ	Mean equiv. cond. Λ	Increase in conductance $\Delta\Lambda$
		0.005-Normal $(NH_4)_2CrO_4$.			
0.0000	0.0006030	0.0000000	120.6		
0.0000	0.0006075	0.0000000	121.5		
0.0000	0.0006050	0.0000000	121.0	121.1	
0.0000	0.0006050	0.0000000	121.0		
0.0000	0.0006060	0.0000000	121.2		2.3
0.0025	0.0006195	0.0000022	123.5		
0.0050	0.0006229	0.0000044	123.7	123.4	
0.0050	0.0006199	0.0000044	123.1		
[0.0100	0.0006230	0.0000089	122.8]		
		0.01-Normal $(NH_4)_2CrO_4$.			
0.0000	0.001163	0.0000000	116.3		
0.0000	0.001166	0.0000000	116.6	116.4	
0.0000	0.001164	0.0000000	116.4		2.0
0.0100	0.001189	0.0000047	118.4	118.4	
0.0100	0.001189	0.0000047	118.4		
		0.02-Normal $(NH_4)_2CrO_4$.			
0.0000	0.002214	0.0000000	110.7	110.7	
0.0000	0.002214	0.0000000	110.7		1.8
0.0200	0.002255	0.0000049	112.5		
0.0200	0.002255	0.0000049	112.5	112.5	
0.0400	0.002260	0.0000100	112.5		
0.0700	0.002265	0.0000150	112.5		
		0.04-Normal $(NH_4)_2CrO_4$.			
0.0000	0.004152	0.0000000	103.8	103.8	
0.0000	0.004152	0.0000000	103.8		1.7
0.0400	0.004225	0.0000052	105.5	105.5	
0.0400	0.004225	0.0000052	105.5		

ductance of unhydrolyzed ammonium chromate. These values were plotted as ordinates, and the cube root of the corresponding concentrations as abscissae, and by extrapolation the value of the equivalent conductance Λ_0 at zero concentration was found to be *141.3* reciprocal ohms. Subtracting the value of the equivalent conductance Λ_{NH_4} of the ammonium ion from this gives as a value for the equivalent conductance Λ_{CrO_4} of the chromate ion *76.9* reciprocal ohms.

The expression on page 1651 for the hydrolysis of ammonium chromate can now be simplified by substituting in it the numerical values for the equivalent conductances of the respective ions to

$$h = \frac{4\Delta\Lambda}{460.8\ \gamma - 104.4},$$

in which $\Delta\Lambda$ is given in the preceding table, and γ is calculable from the conductance values for ammonium chromate.

With the help of the hydrolysis thus obtained the following considera-

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tions will show that it is possible to determine the ionization-constant K_A for the hydrochromate ion. The equilibrium-constants involved in the hydrolysis of ammonium chromate, K_W the ionization-constant for water, K_B that for ammonium hydroxide, and K_A that for the hydrochromate ion may be combined into one constant, the so-called hydrolysis-constant, which equals

$$\frac{K_W}{K_A K_B} = \frac{NH_4OH \times \overline{HCrO_4}}{\overset{+}{N}H_4 \times \overset{=}{CrO_4}}$$

In addition to this equation, which determines the equilibrium, may be formulated the following condition equations:

$$NH_4OH = \overline{HCrO_4} + NH_4HCrO_4$$

$$\overset{+}{N}H_4 = 2\overset{=}{CrO_4} + \overline{HCrO_4}$$

The concentration of ammonium hydroxide is given by the product of the hydrolysis h by the molal concentration C of the ammonium chromate solution; that of the $HCrO_4$-ion is $\frac{1+\gamma}{2}$ times as great[1], γ being the ionization of ammonium chromate at the concentration in question. The concentration of the ammonium-ion in equivalents per cubic centimeter is, as has already been stated, given by the ratio $\frac{\kappa_S}{\Lambda_{o(s)}}$ of the specific conductance of the salt to its equivalent conductance at zero concentration. Taking as values for K_W and K_B, 0.6×10^{-14} and 17.1×10^{-6} respectively[2], values for the ionization constant of the hydrochromate ion were calculated with the help of the above equations.

A summary of the results obtained from the measurements on the hydrolysis of ammonium chromate are given in Table 9.

TABLE 9.

Molal Conc. C	Ionization γ	Hydrolysis h	NH_4OH	$\overline{HCrO_4}$	$\overset{+}{N}H_4$	$\overset{=}{CrO_4}$	$\frac{K_W}{K_A K_B}$	$K_A = \frac{\overset{+}{H} \times \overset{=}{CrO_4}}{\overline{HCrO_4}}$
0.02	0.75	0.029	0.00058	0.000508	0.0298	0.01464	5.75×10^{-4}	5.2×10^{-7}
0.01	0.80	0.029	0.00029	0.000261	0.01593	0.00783	6.05×10^{-4}	5.8×10^{-7}
0.005	0.84	0.030	0.00015	0.000138	0.00838	0.00412	6.00×10^{-4}	5.9×10^{-7}
0.0025	0.875	0.031	0.000078	0.000073	0.00436	0.00214	6.10×10^{-4}	5.8×10^{-7}
							(Mean)	5.7×10^{-7}

Though the values of K_A agree very well with one another, yet on account of the assumptions involved on the theoretical side, and of the sources of error on the experimental side no great accuracy can be claimed for the method.

[1] This follows from the assumption previously made that the unionized fraction of the hydrochromate is equal to one-half of that of the neutral ammonium chromate.

[2] Pub. of the Carnegie Inst., No. 63.

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The Hydrolysis of Ammonium Chromate. Distribution Method.

Experiments by Donald E. Russ.

In this method, which was worked out by Abbott in an investigation soon to be published on the ionization of phosphoric acid, the hydrolysis is measured by determining the concentration of the ammonia produced in the neutral ammonium chromate solution. Briefly the method is this. First the distribution-ratio of ammonia between water and chloroform is found, and afterwards by distribution experiments the concentration of ammonia in chloroform which is in equilibrium with the free ammonia produced by hydrolysis in the aqueous ammonium chromate solution. The product of these quantities equals the desired concentration of ammonia in the ammonium chromate solution.

The procedure followed in determining the distribution ratio is here given. Into each of two bottles was poured about 300 cc. of chloroform and 100 cc. of 1.0-normal ammonia solution, and into each of two other bottles the same quantity of chloroform, but about 200 ccm. of 0.25 normal ammonia solution. The bottles were stoppered and rotated in a thermostat kept constant at 25°, and then left suspended in the thermostat until the layers became clear. From each water layer there was pipetted off 50 cc. portions for analysis. To avoid any loss of ammonia by volatilization each sample was run directly into a measured volume of normal hydrochloric acid known to be in excess, and the excess titrated for with standard ammonia solution, cochineal being used as indicator.

From the chloroform layers there was taken for analysis in the first two cases 100 cc., and in the latter cases 200 cc. of solution. As ammonia is much more soluble in water than in chloroform, any contamination of the chloroform layer with that of the aqueous layer would produce a large error in the distribution ratio. To prevent any such error the device suggested by Abbott was used for removing these portions for analysis. Into the neck of the bottle was inserted a stopper bearing tubes arranged exactly as in an ordinary wash bottle except that the longer tube was sealed at its lower end by a thin bulb. This tube was lowered through the solutions and the bulb broken by forcing it against the bottom of the bottle. The sample of the chloroform layer was then forced up through this tube by means of an air blast into a pipette connected with its upper end. The chloroform solutions thus removed were delivered beneath the surface of about 200 cc. of water contained in a bottle. To the water was added cochineal as indicator and the ammonia determined by titration with 0.1 normal hydrochloric acid and a standard ammonia solution.

The results are tabulated below. In the second column the slight correction for the ionization of the ammonium hydroxide is made.

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TABLE 10.

Conc. NH_3 in H_2O-layer	Conc. Free NH_3 in H_2O-layer C_1	Conc. Free NH_3 in $CHCl_3$-layer C_2	Distribution Ratio $K = C_1/C_2$
0.9624	0.9596	0.03848	24.97
0.9616	0.9588	0.03876	24.84
0.2414	0.2400	0.00963	24.96
0.2404	0.2390	0.00962	24.90
			24.92 (Mean)

In the experiments made to determine the concentration of free ammonia in the ammonium chromate solutions any displacement of the equilibrium due to removal of the ammonia by the chloroform, had to be avoided. Into a one-liter bottle was poured 500 cc. of chloroform and 250 cc. of the ammonium chromate solution under investigation. The bottle was shaken vigorously and then suspended in the thermostat until it had assumed the temperature of 25°. The aqueous layer was then poured off and discarded. A new portion of the ammonium chromate solution was added and the operation repeated. After four repetitions of this character a 400 cc. portion of the chloroform layer was withdrawn and analyzed according to the method already described. The standard hydrochloric acid used in this analysis was 0.01-normal.

The ammonium chromate solutions were prepared, as in the experiments of Merrill, by mixing exactly equivalent amounts of ammonium hydroxide and chromic acid and diluting to the desired volume. It is evident that to thus obtain exact neutrality, very careful analyses of the stock solutions are necessary.

The strength of the stock solution of ammonium hydroxide, free from carbonate, was determined by direct titration against standard hydrochloric solution. According to the experiments and theoretical considerations of Salm[1], the best available indicator to use in the titration of hydrochloric acid with ammonium hydroxide is cochineal, and the best condition is to have the solutions moderately strong. The titration was made accordingly, the stock solutions being about normal.

Since it was the strength of the stock solution of chromic acid as an acid which was desired, the following method for its analysis was employed. To a measured volume of the solution heated to boiling, was added an excess of pure barium acetate dissolved in hot water. The precipitated barium chromate formed was washed four times by decantation through a filter, finally thrown on the filter and washed again. The acetic acid in the filtrate, which never exceeded 200 cc., was determined by titration with a standard barium hydroxide solution, phenolphthalein being used as the indicator. Direct titration in the cold without intermediate filtration was also tried. The end point was sharp, and the results in good accord with the former method. The stock chromic acid solution was about normal in strength.

[1] Z. physik. Chem., 57, 471 (1907).

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The barium hydroxide solution used in the above analysis had been titrated against the hydrochloric acid used in the analysis of the stock ammonium hydroxide solution. By thus referring the analyses of the stock solutions to the same hydrochloric acid solution their relative strengths were accurately determined, and hence absolute neutrality on mixing the calculated volumes more certainly obtained.

Three independent series of experiments were carried out with two strengths of ammonium chromate. In the last case the following test was made as a further check on the absolute neutrality of the ammonium chromate solution.

One hundred cubic centimeters of the solution were digested with solid pure neutral lead sulphate, and the solution decanted through a filter. To the filtrate, which should contain neutral ammonium sulphate formed by the metathesis, was added cochineal. The color indicated neutrality. One drop of a 0.05-normal ammonium hydroxide solution gave the pink color causd by an excess of ammonia, while one drop of a 0.05-normal hydrochloric acid solution gave the orange color characteristic of an excess of acid.

The results or the experiments are given in Table 11. The value of the distribution-ratio used in the calculations was taken equal to *25*.

TABLE 11.

	Molal conc. $(NH_4)_2CrO_4$	Conc. ammonia in $CHCl_3 \times 10^5$	Conc. ammonia in H_2O-solution $\times 10^5$	Hydrolysis
I	0.050	5.51	137.8	0.0276
	0.050	5.33	133.3	0.0267
	0.025	2.67	66.65	0.0267
	0.025	2.70	67.39	0.0270
II	0.050	5.33	133.3	0.0267
	0.050	5.24	131.1	0.0262
	0.025	2.60	65.15	0.0261
	0.025	2.70	67.39	0.0270
III	0.050	5.33	133.3	0.0267
	0.025	2.67	66.65	0.0267

In the formulation of the equilibrium conditions previously given for the calculation of the ionization-constant K_A for the hydrochromate ion from the hydrolysis of ammonium chromate the concentration of the dichromate ions in the solution was neglected. In these stronger solutions especially this concentration, though small, cannot be considered as negligible, and the more exact expressions for the condition equations used in the calculation become,

$$NH_4OH = H\bar{C}rO_4 + 2\bar{\bar{C}}r_2O_7 + NH_4HCrO_4,$$

and

$$\overset{+}{N}H_4 = 2\bar{\bar{C}}rO_4 + H\bar{C}rO_4 + 2\bar{\bar{C}}r_2O_7.$$

The concentration of ammonium hydroxide is known from the distribution experiments; that of the ammonium ions may be estimated by considering it to be equal to that present in the unhydrolyzed ammonium

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chromate solution diminished by the concentration of ammonium hydroxide formed by the hydrolysis. The ionization values used for the computation of the ammonium ion concentration in the unhydrolyzed ammonium chromate solution were calculated from conductivity data obtained by extrapolation on a plot of measurements of Merrill for the conductance of unhydrolyzed ammonium chromate. Though his measurements were made at 18°, no serious error is here involved because of the fact that the ionization of salts changes but little with the temperature. The ionization values used in the calulation were for the chromate solutions, 0.05-molal and 0.025-molal, respectively *0.66* and *0.72*.

The concentration of the dichromate ion in terms of the hydrochromate ion is given by the relation,

$$\overline{\overline{Cr_2O_7}} = K_H \times (\overline{HCr_4O})^2.$$

Since the concentration of the dichromate ion occurs in the above equations only as a small correction term, an approximate value of K_H is sufficient for its estimation. The value used was taken equal to *75*, that obtained from the solubility experiments which follow. The concentration of unionized ammonium hydrochromate may be estimated by assuming, as was done before in the conductivity method, the unionized fraction $(1-\gamma)$ of the ammonium hydrochromate in the mixture to be equal to one-half that of the neutral ammonium chromate; that is for the above concentrations of ammonium chromate *0.17* and *0.14* respectively. The total concentration of ammonium hydrochromate in the mixture may be taken equal to the concentration of ammonium hydroxide.

In Table 12 are presented the results of the calculations. The hydrolysis values used were a mean of those given in the preceding table; the values taken for K_W and K_B at this temperature were 0.8×10^{-14} and 18×10^{-6} respectively[1].

TABLE 12.

Molal conc.	$NH_4OH \times 10^5$	$\frac{1}{NH_4}$	$\overline{HCrO_4} \times 10^5$	$\overline{\overline{Cr_2O_7}} \times 10^5$	$NH_4HCrO_4 \times 10^5$	$\overline{\overline{CrO_4}}$	$\frac{K_W}{K_A K_B}$	K_A
0.05	134.0	0.0647	97.0	7.05	22.8	0.0318	6.3×10^{-4}	7.1×10^{-7}
0.025	66.7	0.0353	53.1	2.11	9.4	0.01736	5.8×10^{-4}	7.7×10^{-7}
							(Mean)	7.4×10^{-7}

The experiments were repeated at 18°. A summary of the results and calculations is given in Table 13. The values for K_B, K_W, K_H, and the distribution-ratio used in the calculations were 1.72×10^{-6}, 0.6×10^{-14}, *30* and *27*[2] respectively.

TABLE 13.

Molal conc. $(NH_4)_2CrO_4$	Hydrolysis	$K_W/K_A K_B$	K_A
0.05	0.0252	5.7×10^{-4}	6.0×10^{-7}
0.025	0.0253	5.4×10^{-4}	6.4×10^{-7}

[1] Pub. of the Carnegie Inst. No. 63.

[2] This value for the distribution-ratio was taken from measurements of Abbott.

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The values of K_A in the above table agree very well with those found by Merrill at the same temperature.

Solubility Experiments with Silver Chromate and Silver Dichromate.

Experiments by Donald E. Russ.

As is the case with all difficultly soluble salts of weak acids the solubility of silver chromate is increased by the presence of acids. This increase of solubility is caused by the decrease in the concentration of the chromate ion in the solution due to its conversion primarily into the hydrochromate ion, and secondarily into the dichromate ion. The increase of solubility is thus a measure of the extent to which these substances are formed. Accordingly the solubility of silver chromate in varying strengths of nitric acid was determined for the purpose of determining the equilibrium-constants for the reactions involved. An interpretation of the results, however, precludes a knowledge of the solubility-product for silver chromate. That this may be calculated from the solubility of silver chromate in an ammonia solution of known concentration the following considerations will show.

The solubility of silver chromate is increased by ammonia in virtue of the formation of the complex salt, $Ag(NH_3)_2CrO_4$. The product of the solubility-product, $K = \overset{+}{Ag}^2 \times \overset{=}{CrO}_4$ for silver chromate by the square of the complex-constant $K_C = Ag(\overset{+}{N}H_3)_2/\overset{+}{A}g \times (NH_3)^2$ for the complex ion $Ag(\overset{+}{N}H_3)_2$ gives an equilibrium equation which must be satisfied in an ammonia solution saturated with silver chromate. This equation solved for the solubility-product for silver chromate gives the expression

$$K = \frac{\overset{=}{CrO}_4 \times [Ag(\overset{+}{N}H_3)_2]^2}{(\overset{+}{N}H_3)^4 \times K^2_C}.$$

In such a saturated solution the concentration of the silver ion is negligibly small due to the fact that the concentration of chromate ions is relatively large and the solubility-product for silver chromate very small. In other words the saturated solution may be considered as consisting entirely of $Ag(NH_3)_2CrO_4$ and free ammonia. The concentrations occurring in the above equation may be very simply calculated from the solubility, S, in mols per liter, the ionization values γ_1 and γ_2 for the complex-salt and the free ammonia in the solution respectively, and the total concentration of ammonia, C. Substituting these quantities in the equation it becomes,

$$K = \frac{4S^3\gamma_1^3}{(1-\gamma_2)^4(C-4S)^4K^2_C}.$$

The complex-constant K_C as determined by Bodländer and Fittig[1] is

[1] Z. physik. Chem., 39, 610 (1902).

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1.47×10^{7}. The solubility of silver chromate in varying concentrations of ammonia solutions was accordingly determined in order to obtain a value for its solubility-product.

The silver chromate used in all of the solubility experiments was prepared by precipitating it from a silver nitrate solution by the addition of potassium chromate solution acidified with acetic acid. The precipitate was washed thoroughly with water.

The procedure employed in the solubility experiments was invariably as follows: To an oil bottle of about 125 cc. capacity was added moist solid silver chromate to a depth of about one-half an inch, and then the desired ammonia solution until nearly filled. The bottle was corked and rotated in the thermostat at 25° for a short while, then opened, and the solution poured off and replaced by a new portion of the same strength. By this means the silver-chromate was freed of any possible impurity and a solution of ammonia of exactly the desired concentration introduced. Equilibrium was approached from supersaturation as well as undersaturation. After rotating for from two to four hours to reach equilibrium the bottle was suspended in the thermostat to allow the precipitate to settle, and 50 or 100 cc. pipetted off through cotton filters for analysis.

The solution was acidified with nitric acid and the silver precipitated as the chloride by the addition of potassium chloride in slight excess. After heating to boiling, the silver chloride was filtered on a Gooch crucible, washed, thoroughly dried, and weighed. The chromate in the filtrate was determined volumetrically by adding an excess of potassium iodide, and, after standing five minutes to allow the reaction to complete itself, titrating for the iodine liberated with 0.05-normal sodium thiosulphate. Starch solution was added only after the brown color of the free iodine had almost disappeared, and the titration continued to a disappearance of the blue color. The thiosulphate was standardized against potassium dichromate, the conditions followed being those used in the analysis.

In Table 14 are presented the results of the measurements and calculations.

TABLE 14.

Conc. NH_4OH C	Solubility (Volumetric) $S \times 10^3$	Solubility (Gravimetric) $S \times 10^3$	Mean Solubility $S \times 10^3$	γ_1	$1 - \gamma_2$	$C - 4S$	$K = \frac{4S^3\gamma_1^2}{(1-\gamma_2)^4(C-4S)^4K'_c}$
0.01	2.003	2.000					
0.01	2.010	2.005	2.004	0.91	0.91	0.001984	10.5×10^{-11}
0.02	4.165	4.170					
0.02	4.171	4.170	4.169	0.88	0.93	0.003324	10.0×10^{-11}
0.04	8.580	8.585					
0.04	8.587	8.625	8.595	0.84	0.95	0.005620	8.6×10^{-11}
0.08	17.57	17.58					
0.08	17.57	17.58	17.58	0.79	0.96	0.00968	6.6×10^{-11}
						(Mean)	8.9×10^{-11}

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The values for the ionization γ_1 of the complex salt were obtained by assuming its ionization to be the same as that of potassium sulphate at the same concentration; those for the ionization γ_2 of the free ammonium hydroxide were calculated from the ionization-constant for ammonium hydroxide. The value of the solubility-product for silver chromate used for the subsequent calculation was taken equal to 9×10^{-12}. Except as otherwise indicated in the table the procedure followed in determining the solubility of silver chromate in nitric acid solutions was identical with that given above both as to the attainment of equilibrium and as to analysis of the saturated solutions. In the table giving the results of the measurements *u* signifies that equilibrium was approached from undersaturation, *o* from supersaturation. The concentrations of chromium and silver in the saturated solutions are expressed as milli-atomic in chromium and silver respectively.

TABLE 15.

	Conc. HNO_3	Conc. Total Chromium	Conc. Total Silver
I	0.01 (*u*)	3.157	6.312
	0.01 (*o*)	3.158	6.318
	0.015 (*u*)	3.730	
	0.02 (*u*)	4.177	8.356
	0.02 (*o*)	4.177	8.356
	0.025 (*u*)	4.567	
	0.03 (*u*)	5.200	
	0.04 (*u*)	5.800	11.62
	0.04 (*o*)	5.807	11.62
	0.05 (*u*)	6.380	
	0.06 (*u*)	6.833	
	0.07 (*u*)	7.333	
	0.075 (*u*)	7.477	
	0.075 (*u*)		14.85
II[1]	0.08 (*u*)	7.260	15.46
	0.08 (*o*)	7.260	15.45
	0.10 (*u*)	5.647	19.00
	0.10 (*o*)	5.647	19.02
	0.13 (*u*)	4.293	23.89
	0.13 (*o*)	4.296	23.90
	0.14 (*u*)	3.948	25.63
	0.14 (*o*)	3.948	25.63

[1] Shaken for three days.

An inspection of Table 15 shows that in the nitric acid solutions less than 0.08-normal the concentration of silver in the saturated solution is double that of the chromium, the proportions in which the two elements are present in silver chromate, while in the nitric acid solutions above 0.075-normal the concentration of dissolved chromium decreases, and that of silver increases with the increasing concentration of the acid. A consideration of the equilibrium equations will show that this phenomenon can be readily explained by the fact that the solubility-product for silver dichromate has been reached, and that this salt has begun to separate out as a second solid phase.

In order to be sure that this second solid phase really was silver dichro-

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mate and not possibly the silver hydrochromate some of it was prepared and analyzed. It was made by adding chromic acid and silver nitrate in about equivalent amounts to form silver dichromate to a nitric acid solution about 0.1 normal. Under these conditions no silver chromate should precipitate. The precipitate was filtered and washed with nitric acid solution about 0.1 normal. One portion was dried at 110°, and a second portion was left for four days in a vacuum desiccator over sulphuric acid. Both samples were analyzed for their silver content. The first two results in the table refer to the sample dried at 110°, the other two to that dried in the desiccator. A comparison of the figures shows conclusively that the salt was silver dichromate.

TABLE 16.

Gms. Salt Analyzed.	Gms. AgCl Expm't Found	Gms. AgCl Calc. for $Ag_2Cr_2O_7$	Gms. AgCl Calc. for $AgHCrO_4$
1.0821	0.7188	0.7178	0.6893
1.1139	0.7385	0.7389	0.7098
1.523	1.0090	1.010	0.9703
1.8341	1.2171	1.216	1.169

A quantitative consideration of the foregoing results will be taken up in connection with the next series of solubility measurements. These experiments consisted in shaking pure silver dichromate, prepared as described above, with water, with nitric acid solutions of varying concentrations, and finally with a solution containing definite amounts of both nitric acid and silver nitrate till equilibrium was reached, and then analyzing the respective solutions for their content in silver and chromium. The method of establishing an equilibrium and of analysis was the same as that already described. The results of the measurements are given in Table 17. As before the concentrations of chromium and silver are expressed as milli-atomic.

TABLE 17

	Conc. HNO_3	Conc. $AgNO_3$	Total Conc. Chromium.	Total Conc. Silver.
I*	0.00	0.00	32.20	5.385
	0.00	0.00	32.19	5.395
	0.01	0.00	25.06	6.127
	0.01	0.00	25.06	6.135
	0.02	0.00	20.21	7.145
	0.02	0.00	20.21	7.152
	0.04	0.00	13.59	9.524
	0.04	0.00	13.59	9.524
II	0.06	0.00	11.10	11.10
	0.06	0.00	11.10	
	0.08	0.00	11.11	11.10
	0.08	0.00	11.10	
	0.08	0.01	6.625	
	0.08	0.01	6.623	

*Shaken for three days.

In the nitric acid solutions 0.06 normal and stronger the concentration of the chromium is seen to be equal to that of the silver, while in the less dilute solutions of nitric acid the concentration of the chromium ex-

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ceeds that of the silver. The explanation of this is that with water and the more dilute nitric acid solutions, some of the solid silver dichromate is converted to solid silver chromate with the formation of the excess of chromium in the solution, while with the nitric acid solutions above 0.04 normal there is but one solid phase, silver dichromate, in equilibrium with the solution.

The discussion of the results of all of the solubility experiments with the chromates of silver in nitric acid divides itself most naturally into three parts. First will be considered the case in which silver chromate alone is in equilibrium with the solution, second that in which both silver chromate and silver dichromate are present as solid phases, and third that in which silver dichromate alone constitutes the solid phase.

In each case, before any final quantitative interpretation of results could be made, it was necessary to estimate the concentration of all unionized substances present in the respective solutions in appreciable amount. Here as in the freezing-point experiments of Eaton, the concentration of any HCr_2O_7-ion or of unionized $AgHCr_2O_7$ was neglected. It is also to be noted that in every solution, due to the relatively large concentration of the hydrogen ion, that of the chromate ion, and hence also that of unionized silver chromate can be considered as negligibly small in comparison with those of the other substances. The unionized substances in the solutions whose concentrations were considered were $AgNO_3$, $AgHCrO_4$, $Ag_2Cr_2O_7$, HNO_3, H_2CrO_4, and $H_2Cr_2O_7$. In computing these concentrations the principle suggested by Noyes[1] that the ionization-constant[2] for salts is a function of the total ion-concentration of the solution and that alone, and that salts of the same type have at equal ion-concentrations the same value of the ionization-constant, was followed. The ionization-constant for silver hydrochromate was considered to be equal to that for silver nitrate at the same ion-concentration, that for silver dichromate and dichromic acid as equal to that for potassium sulphate, and that for chromic acid as equal to that for nitric acid.

The method of making these computations was briefly this. First with the help of the experimental data and of the formulation given later, and neglecting the concentration of all unionized substances, the concentration of the dichromate and the hydrochromate present was estimated. Next a guess was made as to the concentration of each of the ions present, and from these the total ion-concentration in the solution roughly determined. Then the ionization-constants for silver nitrate, potassium sulphate, and nitric acid respectively in solutions with this ion-concentration were calculated from the conductivity data of Kohlrausch for these substances alone. Finally these approximate ion-concentrations in the solu-

[1] Science 20, 584 (1904); Z. physik. Chem., 52, 635 (1905).

[2] The term ionization-constant here signifies the ratio of the product of the concentrations of the two ions of the salt to that of its unionized part.

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tion were substituted in the expression for the ionization-constant, and using the corresponding value for the ionization-constant above obtained, the concentration of each of the unionized substances was calculated. From the experimental data, the concentration of the total silver, of the total chromium, and of the total nitrate in each solution were known. By deducting the corresponding concentrations of the unionized substances from each of these values, were obtained for the concentration of the silver ion, that of chromium in the form of ions, and that of the nitrate ion. To gain separate values for the concentration of the hydrochromate ion and of the dichromate ion the formulation which follows was resorted to. The concentration of the hydrogen ion was calculated from the relation that the sum of the equivalent concentration of the cathions must equal that of the anions.

Having now obtained these more accurate values for the concentrations of each of the ions present, the whole process was repeated. An idea as to their nearness to the truth according to this principle may be obtained by observing how much the repetition changes the respective concentrations.

From the above estimation of the concentrations of the unionized substances present, there is known in each solution the concentration, $\overset{+}{Ag}$, of the silver ion, that, $\overset{+}{H}$, of the hydrogen ion, and the sum, $\overset{-}{HCrO_4} + 2\overset{=}{Cr_2O_7}$, of the hydrochromate ion concentration and twice that of the dichromate ion. In addition to these conditions of concentration there must be satisfied for the different cases certain equilibrium equations. For the first case, that in which silver chromate is the single solid phase, these equilibrium equations are:

$$K_1 = \overset{+}{Ag}^2 \times \overset{=}{CrO_4}$$

$$K_A = \frac{\overset{+}{H} \times \overset{=}{CrO_4}}{\overset{-}{HCrO_4}}$$

$$K_H = \frac{\overset{=}{Cr_2O_7}}{(\overset{-}{HCrO_4})^2}$$

For the case in which silver dichromate also saturates the solution the additional equation, the solubility-product K_2 for the silver dichromate is obtained;

$$K_2 = \overset{+}{Ag}^2 \times \overset{=}{Cr_2O_7}.$$

For the third case, that in which silver dichromate is the only solid phase, the solubility-product of the silver chromate is of course not involved, and since the ionization of the hydrochromate formed by the hy-

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dration of the dichromate ion is prevented by the excess of acid present, its ionization-constant likewise need not be considered.

Since the value of the solubility-product K_1 for silver chromate has already been determined, it is evident that for the first case, if one of the constants, K_A or K_H, is given, the other may be calculated; or, if the known concentration conditions for any pair of these solutions are combined with the equilibrium equations it is possible to calculate values of both K_A and K_H.

Similarly for the second case, given one of the three constants K_A, K_H, or K_2, the others can be calculated, or from a consideration of any pair of solutions, values of all of these constants can be found.

Analogous considerations hold for the third case. It is to be noted here that the solubility, and hence the relative amounts of hydrochromate and dichromate in the solution are not much affected by increasing the concentration of the nitric acid. Addition of silver nitrate, a salt with a common ion, does, however, produce the desired effect. The values of the hydration-constant K_H, and the solubility-product K_2, for silver dichromate obtained from a consideration of pairs of solutions, would in this case be independent of any value for the ionization-constant K_A, for the hydrochromate ion.

A consideration of Table 18, which contains the final results of the calculations, shows that for the solutions obtained by shaking silver chromate with nitric acid, the concentration of the hydrochromate ion is large as compared with that of the dichromate ion. This signifies that the secondary reaction, the dehydration of the hydrochromate ion to form dichromate ion, plays but little part in producing the equilibrium conditions, and hence only an approximate value of the hydration-constant K_H is necessary to calculate a fairly reliable value for the ionization-constant K_A. The solutions which contain the dichromate ion in relatively the largest amount, and hence which provide the best data for calculating the most reliable value for the hydration-constant, are, as seen from the table, those obtained by shaking silver dichromate with water, and with nitric acid solutions so dilute as to cause separation of the second solid phase, silver chromate.

These considerations furnish the reasons for the method followed in calculating the results tabulated. For the first case by combining the conditions of concentration existing in solutions varying most widely in their chromium content, the first and fourth given in the table, with the equilibrium equations, were calculated values for both K_A and K_H. The values thus obtained were 5.5×10^{-7} and 21 respectively. Assuming this value for K_H, values of K_A were calculated from the concentration conditions prevailing in the second and third solutions. A mean of all values for the ionization-constant so obtained was then taken and used to

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calculate values for the hydration constant from the ninth, tenth, eleventh and twelfth solutions.

A mean of these gave a more accurate value for the hydration-constant to use with the original first four solutions in order to obtain a new, more reliable value for the ionization-constant. By working back and forth according to this principle the values tabulated were obtained. In the table the constants enclosed in the parentheses were assumed in order to calculate the other constants given.

The constants agree well among themselves. Though perhaps the assumptions made in the various calculations do not warrant such a comparison, yet it is seen from the results that the value for the hydration-constant K_H obtained at this temperature is as might be expected somewhat greater than that found by Eaton at 0°. The values for the ionization-constant K_A also agree well with those obtained from the experiments on the hydrolysis of ammonium chromate.

Discussion of the Results in Relation to Those of Other Investigators.

The measurements of Whetham[1] on the conductance at 0° of solutions of potassium dichromate are also in accordance with the results here presented. The following table derived from his measurements gives a comparison of the increase in the equivalent conductance observed for solutions of potassium dichromate between certain concentrations with the corresponding increase for solutions of potassium chloride and barium chloride.

Conc. Interval.	$\Delta\Lambda(K_2Cr_2O_7)$	$\Delta\Lambda(KCl)$	$\Delta\Lambda(BaCl_2)$
0.1 — 0.01	6.1	5.3	8.8
0.01 — 0.001	1.0	2.4	5.4
0.001 — 0.0001	10.9	0.7	2.3

In the first concentration-interval the change for the dichromate lies between that for the other two, in the second it is much smaller than either, and in the third it is very large compared with either of the other two. The abnormally small increase at first in the equivalent conductance is, as previously mentioned, probably due to the conversion of the dichromate ion into the slower moving hydrochromate ion, and the rapid increase in the very dilute solution to the ionization of the latter into hydrogen ion and the doubly charged chromate ion. This may be seen from a consideration of the freezing-point results of Eaton (See Table 5). These indicate that at 0° in a 0.1 normal solution of potassium dichromate the molal concentration of the dichromate ion is nearly equal to that of the hydrochromate ion, while in a 0.02 normal solution the ratio

$Cr_2O_7^=/HCrO_4^-$ of their concentrations is only 1/2. Approximate calculations neglecting the unionized parts of salts, and using *50* as an approximate

[1] Pr. Roy. Soc., 71, 332 (1903).

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TABLE 18.

Solid phases	Conc. HNO_3	Ag × 10^5	$HCrO_4^-$ × 10^4	$Cr_2O_7^=$ × 10^5	H^+ × 10^3	$AgNO_3$ × 10^3	$AgHCrO_4$ × 10^3	$Ag_2Cr_2O_7$ × 10^5	HNO_3 × 10^2	H_2CrO_4 × 10^2	$H_2Cr_2O_7$ × 10^3	K'_A × 10^7	K_2 × 10^7	K_H
Ag_2CrO_4	.01	5.808	2.245	0.3775	6.661	0.392	0.112	0.0012	0.1395	0.04	0.0014	7.9		(75)
	.02	7.488	2.775	0.577	15.15	0.730	0.134	0.0019	0.562	0.1034	0.0038	8.7		(75)
	.04	10.02	3.530	0.935	32.34	1.410	0.176	0.0032	1.63	0.2035	0.0103	8.2		(75)
	.075	12.41	4.220	1.333	62.94	2.345	0.193	0.0041	4.21	0.3465	0.0212	8.7		(75)
Ag_2CrO_4 and $Ag_2Cr_2O_7$	.08	12.64	4.120	1.273	66.73	2.62	0.195	0.004	4.68	0.349	0.021	9.1	2.0	(75)
	.10	15.29	3.410	0.8705	80.29	3.55	0.172	0.0027	6.02	0.292	0.0142	9.1	2.0	(75)
	.13	18.88	2.745	0.5640	101.2	4.88	0.141	0.0018	8.95	0.258	0.010	9.3	2.0	(75)
	.14	20.21	2.570	0.4965	107.7	5.29	0.131	0.0016	10.3	0.249	0.009	9.2	2.0	(75)
	.00	5.009	11.06	9.910	25.87	0.000	0.304	0.039	0.000	0.555	0.193	(8.4)	2.5	81
	.01	5.554	9.627	7.151	27.72	0.228	0.292	0.028	0.405	0.518	0.141	(8.4)	2.2	77
	.02	6.337	8.416	5.392	31.54	0.492	0.272	0.024	0.826	0.456	0.115	(8.4)	2.1	76
	.04	8.162	6.707	3.042	41.70	1.095	0.243	0.013	1.835	0.407	0.065	(8.4)	2.0	68
$Ag_2Cr_2O_7$	.06	9.26	5.610	2.365	56.18	1.61	0.209	0.0099	3.28	0.424	0.0594		2.0	(75)
	.08[1]	13.47	3.855	1.117	74.36	2.98	0.172	0.0045	5.28	0.304	0.0256		2.0	(75)

[1] This last nitric acid solution was also 0.01 normal with respect to silver nitrate.

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value for the hydration constant show that in a solution 0.001 normal this ratio is reduced to 1/20. These changes in the relative concentrations of the dichromate ion and hydrochromate ion, doubtless account for the small change in the equivalent conductance within the concentration interval of 0.1 — 0.001 normal. It is true that the ionization of the hydrochromate ion throughout this range of concentration is not entirely negligible; for example, in a 0.02 normal solution where the concentration of the hydrochromate ion is 0.009, its ionization calculated from $K_A = 7 \times 10^{-7}$ is almost one per cent.; but the much larger change in the proportion of hydrochromate ion and dichromate ion overbalances this. In the solutions more dilute than 0.001 normal the chromium is almost wholly present as hydrochromate ion, and the ionization of this rapidly becomes considerable, and, as above stated, accounts for the abnormally high conductance of the solutions. On account of these superimposed effects no quantitative interpretation of the results was attempted.

Sand and Kaestle[1] and Spitalsky[2] have investigated the constitution of chromates in solution by determining the concentration of the hydrogen ion in various chromate mixtures. The work of Spitalsky is of interest inasmuch as he takes into consideration the presence of the hydrochromate ion. The two reactions which he considers as determining the equilibria in chromate solutions are :

$$\overline{\overline{Cr}}_2O_7 + H_2O = 2\overline{\overline{CrO}}_4 + 2\overset{+}{H}, \text{ and } \overset{+}{H} + \overline{\overline{CrO}}_4 = H\overline{CrO}_4.$$

The method employed by him for measuring the concentration of the hydrogen ion was to determine the rate at which diazoacetic ester was catalytically decomposed by the different chromate solutions. Bredig and Fraenkel[3] have shown this to be a first order reaction, and that its rate is proportional to the concentration of the hydrogen ion.

From the concentration of the hydrogen ion thus found in two solutions of potassium dichromate, 0.0169 and 0.0302 molal respectively, Spitalsky calculates what he considers his best values for the equilibrium-constants of the above cited reactions. They are

$$K_1 = \frac{\overset{+}{H}^2 \times (\overline{\overline{CrO}}_4)^2}{\overline{\overline{Cr}}_2O_7} = 5.1 \times 10^{-15} \text{ and } K_A = \frac{\overset{+}{H} \times \overline{\overline{CrO}}_4}{H\overline{CrO}_4} = 2.7 \times 10^{-7}$$

The ionization-constant K_A is of the same order of magnitude as that found by us, 8×10^{-7}. The ratio (K_A^2/K_1) of the square of the latter constant to the former one, however, gives a value for the hydration-constant K_H equal to *0.014*, which is not at all in accord with the value (*75*) given above. The discrepancy is due to the fact that serious error

[1] Z. anorg. Chem., 52, 101 (1907).

[2] Ibid., 54, 265 (1907).

[3] Z. physik. Chem., 60, 202 (1907): Z. Electrochem., 11, 525.

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was introduced into his calculation by the approximate assumptions that were made.

In order to determine how far our constants are in accord with Spitalsky's results, I have made certain calculations for four of the dichromate solutions investigated by him. The results are tabulated below.

By making the same assumptions as to the ionization relations in potassium dichromate solutions as were presented in detail under the freezing-point experiments of Eaton, and taking *75* as the value for the hydration constant K_H, the concentrations were calculated which are given in the fourth, fifth, sixth and seventh columns of the table. Since in a potassium dichromate solution the concentration of the chromate ion may be placed equal to that of the hydrogen ion[1], the relation holds that

$$\overset{+}{H}^2 = K_A \times \overset{-}{HCrO_4}.$$

With the help of this equation taking K_A equal to 8×10^{-7}, the values of the hydrogen ion recorded in the next to the last column were calculated.

Conc. Total Cr.	Ionization $K_2Cr_2O_7$ (γ_1)	Ionization $KHCrO_4$ (γ_2)	Conc. $KHCrO_4$	Conc. $K_2Cr_2O_7$	Conc. $\overset{=}{Cr_2O_7}$	Conc. $\overset{-}{HCrO_4}$	Conc. $\overset{+}{H}$ (calc.)	Conc. $\overset{+}{H}$ (Obs.)
0.0338	0.795	0.905	0.00113	0.00225	0.00870	0.01077	0.000093	0.000095
0.0604	0.755	0.882	0.00198	0.00535	0.01647	0.01482	0.000109	0.000127
0.0964	0.722	0.861	0.00306	0.01035	0.02688	0.01893	0.000123	0.000170
0.1208	0.705	0.850	0.00374	0.01414	0.03377	0.02122	0.000130	0.000188

A comparison of the hydrogen ion concentrations thus calculated with those observed by Spitalsky (given in the last column) shows that there is nearly complete agreement in the most dilute solutions, and that even in the more concentrated solutions, where the quantities of the unionized substances are larger, the agreement is still a tolerable one[2], considering the estimates that were made in the computation of K_A.

Spitalsky in the interpretation of all of his results has underestimated the importance of the reaction, $\overset{+}{H} + \overset{=}{CrO_4} = \overset{-}{HCrO_4}$, in determining the condition of chromates in solution. Thus his conclusion that in dilute solutions of potassium dichromate the concentration of the $HCrO_4$-ion is very small as compared with that of the Cr_2O_7-ion, is neither in accordance with the above calculations (see for example, the preceding table) nor consistent with the constants given by him. Thus, the concentra-

[1] Assuming that any unionized K_2CrO_4 formed is compensated by the $\overset{-}{HCr_2O_7}$, H_2CrO_4, and H_2Cr_2O, formed, or that all of these quantities are negligible.

[2] Reference should, however, be made to the remarkable fact that the observed hydrogen-ion-concentration seems to be proportional to the concentration of the hydrochromate ion instead of to its square root. There seems to be no other explanation of this than that it arises from error in the assumption that $\overset{+}{H} = \overset{=}{CrO_4}$ especially in the more concentrated solutions where any estimate of the quantities of various unionized substances that may be produced, is very uncertain.

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tion of the $HCrO_4$-ion in the potassium dichromate solution 0.0338-atomic in chromium calculated by substituting the hydrogen-ion concentration observed by him, and his value for the ionization-constant K_A in the expression $\overset{+}{H}^2 = K_A \times \overline{HCrO_4}$ is equal to 0.03342; that is, essentially all of the chromium is in the form of hydrochromate. Furthermore, if this did represent the constitution of the solution, the concentration of the Cr_2O_7-ion would be so small as to render its estimation by difference, and hence the evaluation of the hydrolysis-constant given by Spitalsky, very inaccurate.

Similarly Spitalsky concludes from the fact observed by him that in solutions of chromic acid the concentration of the hydrogen ion is essentially equal to that of the total chromium, that chromic acid exists as $H_2Cr_2O_7$ dissociating into only H-ion and Cr_2O_7-ion. This fact is equally well explained by assuming the existence of H_2CrO_4 dissociating into H-ion and $\overline{HCrO_4}$-ion. The ionization of the very weak acid ion, $\overline{HCrO_4}$, would be entirely prevented by the presence of the H-ion resulting from the primary ionization. As already pointed out, both hydrochromate and dichromate exist simultaneously in a proportion dependent on the concentration of the solution.

According to Spitalsky's results, the addition of potassium dichromate to chromic acid is analagous to the addition of potassium chloride to hydrochloric acid, and affects but little the concentration of the hydrogen ion. On the other hand, the addition of a small proportion of potassium chromate to chromic acid solutions removes quantitatively the hydrogen ion from the solution, primarily with formation of the weak acid anion, $\overline{HCrO_4}$. Whether or not this hydrochromate ion remain as such, or be partly or wholly converted to dichromate ion through dehydration, would be without influence on the hydrogen ion concentration. Similarly the concentration of hydrogen ion in a potassium dichromate solution is largely decreased by the addition of a very small proportion of potassium chromate, owing to the formation of hydrochromate. These facts afford therefore, no confirmation of Spitalsky's interpretation since they are equally in accordance with the assumption of a large proportion of hydrochromate ion.

Summary.

In this article the view has been suggested and substantiated that in the equilibria prevailing in chromate solutions the intermediate hydrochromate ion plays an important part, the main equilibria involved being those of the reactions:

$$\overline{\overline{CrO_4}} + \overset{+}{H} = \overline{HCrO_4} \text{ and } 2\overline{HCrO_4} = H_2O + \overline{\overline{Cr_2O_7}}.$$

The relative amounts of chromate, hydrochromate, and dichromate

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present are dependent upon the composition of the mixture and its concentration, and on the values of the equilibrium-constants for the two reactions.

Freezing-point determinations were made with solutions of chromic acid and of potassium dichromate varying in concentration from about 0.02 to 0.1 atomic in chromium. The observed lowering of the freezing-point in the most dilute solutions was actually greater than that which would correspond to complete ionization of these substances into dichromate ion and hydrogen ion or potassium ion, the van't Hoff factor i reaching *3.33* and *3.24* at the lowest concentrations, thus indicating the existence of hydrochromate ions in appreciable amount. From the results, approximate values of the equilibrium-constant for the second reaction, *i. e.* of the hydration-constant $K_H = \bar{Cr_2O_7}/(\bar{HCrO_4})^2$ were calculated. The values of this constant obtained from the potassium dichromate and chromic acid experiments are *61* and *27*, respectively.

The hydrolysis of ammonium chromate in dilute solutions was determined by two methods. The hydrolysis was assumed to be due mainly to the formation of ammonium-hydroxide and hydrochromate, the small amount of dichromate formed being subsequently taken into account as a correction term in the evaluation of the ionization-constant for the hydrochromate ion. In the first method the hydrolysis was derived from the increase in the conductance of a neutral ammonium chromate solution caused by the addition of enough ammonia to completely drive back the hydrolysis; and in the second method it was determined by distribution experiments from the concentration of ammonia in chloroform which was in equilibrium with the ammonium chromate solution in question. The distribution-ratio at 25° of ammonia between water and chloroform was incidentally determined, and found to be *25*.

The values for the ionization-constant $K_A = \overset{+}{H} \times \bar{CrO_4}/\bar{HCrO_4}$ at 18° obtained by the two methods were 5.7×10^{-7} and 6.2×10^{-7} respectively, and that at 25° by the distribution method 7.4×10^{-7}. The constant is therefore only about 1/30 as great as that of acetic acid. Correspondingly, ammonium chromate in 0.05 molal solution was found to be *2.7* per cent. hydrolyzed.

The solubility at 25° of silver chromate in dilute ammonia solutions was determined, and from the results and the value of the complex-constant for the silver-ammonia-cation by application of the mass-action law, a value for the solubility-product, $(\overset{+}{Ag})^2 \times \bar{CrO_4}$, for silver chromate was calculated. The value obtained was 9×10^{-12}, the corresponding silver-ion concentration in the saturated solution in water being 2.5×10^{-4} mols. per liter.

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Solubility experiments at 25° were also made by shaking solid silver chromate with nitric acid solutions varying in concentration from 0.01 to 0.14 normal, and solid silver dichromate with water, with nitric acid solutions from 0.01 to 0.08 normal, and with an 0.08 normal nitric acid solution which was also 0.01 normal with respect to silver nitrate. In the experiments both the total silver and total chromium were analytically determined. The results showed that silver chromate in acid solutions stronger than 0.075 normal, is decomposed with separation of silver dichromate as a second solid phase. Correspondingly silver dichromate is decomposed by water and nitric acid solutions more dilute than 0.06 normal, with separation of solid silver chromate.

From these results and the solubility product for silver chromate above given values for the other equilibrium-constants involved, were calculated, namely the hydration-constant K_H, the ionization-constant K_A, and the solubility-product $K = (\overset{+}{Ag})^2 \times \overset{=}{Cr_2O_7}$ for silver dichromate. The final values obtained in this way for these three constants were $K_H = 75$, $K_A = 8.4 \times 10^{-7}$, and $K = 2 \times 10^{-7}$, respectively. This value of the solubility product corresponds to a silver concentration of 7.3×10^{-3} mols. per liter.

In the computation of these constants the concentrations of the unionized substances present in the solutions were estimated according to the following principle proposed by Noyes.[1] The ratio of the product of the concentration of the two ions of a salt to that of its unionized part is a function of the sum of the equivalent concentrations of all ions in the solution and of that alone; and further, that this ratio is for any given ion-concentration approximately the same for salts of the same ionic type. Potassium sulphate was taken as a typical tri-ionic salt, and silver nitrate (or potassium chloride) as a typical di-ionic one. The ionization relations of dichromic acid $H_2Cr_2O_7$ were considered like those of potassium sulphate, while chromic acid H_2CrO_4 with respect to the dissociation of its first hydrogen was considered analogous to nitric acid. On account of these assumptions involved in their calculation, no great accuracy can be claimed for the values of the constants. The values obtained by the different methods do, however, agree well with one another, and verify the underlying conception that the hydrochromate ion is one of the important constituents of chromate solutions. With respect to the proportion of this ion present, it is of interest to note that the results lead to the conclusion that in a 0.1 molal solution of potassium dichromate, approximately 15 per cent. of the salt exists as hydrochromate and 85 per cent. as dichromate, while in a 0.01 molal solution approximately 45 per cent. exists in the former state.

[1] Science, 20, 584 (1904); Z. physik. Chem., 52, 635 (1905).

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It has also been shown that the results of Whetham on the conductivity of potassium dichromate and those of Spitalsky on the catalysis of diazoacetic ester by chromate solutions are in substantial accord with the results from this investigation, and that the conclusion drawn by Spitalsky that his experiments indicated that the hydrochromate ion is not present in any considerable quantity in dilute solutions of chromic acid and potassium dichromate is an erroneous one.

In conclusion, I wish to thank Prof. A. A. Noyes for suggesting this investigation and for his ever-willing advice throughout its execution.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
Boston, September, 1907.

THE PERMEABILITIES OF COLLODION, GOLD BEATER'S SKIN, PARCHMENT PAPER AND PORCELAIN MEMBRANES.

BY S. LAWRENCE BIGELOW.

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Contents.

The object and scope of the investigation. Previous investigations. Apparatus. Method of measurement. The unit of permeability. The effect of changing the pressure upon the permeability of collodion, of gold beater's skin, of parchment paper, of porcelain. The results of the pressure experiment's and Poiseuille's formula. Permeability of collodion at different temperatures. Calculation to test the applicability of Poiseuille's formula. The effect of changing the temperature upon the permeability of parchment paper, of porcelain. Discussion of results and theory. Summary.

The Object and Scope of the Investigation.

Probably it will be conceded, without the presentation here of a summary, which, even if abbreviated until inadequate, would require too much space, that there are numerous theories, each accounting ingeniously for some of the facts included under the comprehensive title of osmotic phenomena and conflicting with others. One cause for the lack of unanimity of opinion on even the most fundamental propositions, such as the function of the membrane in an osmotic cell, is the number of unknown quantities in each single experiment. Unless we have a solvent, a solute, and a membrane, there is no osmosis in the ordinary sense of the term, but with all three present the number of possible interactions is large. It has seemed to the writer that results could be obtained, which might have an interesting bearing upon the problems of osmosis, by omitting the solute. The attention is thereby fixed on the function of the membrane.

My intention is to force a pure liquid (solvent) through several different membranes at different pressures and at different temperatures, and to force different pure liquids through one and the same membrane at different pressures and temperatures. After numerical values for these processes have been established, solutions may be put through the same treatment with some hope of elucidating valuable

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facts. It may be objected that the results obtained by "filtration under pressure" are different from those obtained by "dialysis", in fact Bechhold[1] in a recent article has shown to what extent this may be the case. But it by no means follows that results by "filtration" methods will be valueless in the interpretation of osmotic phenomena. The present article deals with the first division of the above program and contains an account of experiments upon the passage of water through collodion, gold beater's skin, parchment paper and porcelain at different pressures and temperatures.

Previous Investigations.—The literature bearing directly upon the specific problem, the passage of pure liquids through membranes at different pressures and temperatures, is not extensive. W. Schmidt[2] determined the rates at which water and several salt solutions passed through different animal membranes, at different pressures and temperatures. He made some interesting observations which at the same time illustrate the difficulty of securing concordant results in such work. For instance, he found that of two pieces cut from the same pig's bladder or pericardium of a cow, one would permit the passage of water three times as rapidly as the other. He found a marked difference resulted when he reversed a membrane and forced the water through in the opposite direction. In some cases the volume of water which passed in a given time was increased ten-fold by such reversal. He says this is not due to the internal structure but to differences in the tension upon the membrane, as put on its holder. Matteucci and Cima[3] in 1845 found similar differences in osmotic effects dependent on which surface of the skin of a frog, of an eel, and of other animals, was presented to the solution and which to the pure solvent. Schmidt found that a membrane allowed to dry out showed a lessened permeability in consequence. He varied his pressures only within narrow limits, in one series between 0.613 and 1.721 meters of water, and found that the amount of water driven through was almost but not quite, proportional to the pressure. He also varied the temperature within narrow limits, in one series between 11.8° and 24.8°. He inserted his values in Poiseuille's formula for the passage of liquids through capillary tubes, and having calculated new constants for the formula, decided that it applied. It would be rash to conclude from Schmidt's results alone, that the passage of liquids through animal membranes followed Poiseuille's law, as his apparatus was crude, his temperatures were calculated through a complicated series of corrections, his pressure and temperature ranges were small and his experiments few. A

[1] Kolloidstudien mit der Filtrations methode. Z. physik. Chem., 60, 257-318 (1907).

[2] Versuche über Filtrationsgeschwindigkeit verschiedener Flüssigkeiten durch thierische Membranen. Pogg. Ann., 99, 337-88 (1856).

[3] Mémoire sur l'endosmose. Ann. chim. phys. 13, [3], 63-86 (1845).

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large part of Schmidt's work was upon solutions, the consideration of which does not come within the scope of this article.

Guerout[1] forced water through bladder, gold beater's skin and parchment paper membranes. Details as to his experimental methods are almost entirely lacking. He says that while the structure is doubtless something different, it is nevertheless possible to imagine all the capillaries in a membrane as prismatic tubes, perpendicular to the faces of the membrane. Making this assumption, and applying Poiseuille's formula, he calculated the average diameter of the pores in bladder as between 0.000014 and 0.000020 mm; in gold beater's skin as between 0.000008 and 0.0000175 mm. and in parchment paper as between 0.000021 and 0.000026 mm. He confirmed his results by forcing water through a bundle of fine steel wires, the open spaces in which he calculated, from microscopic measurements, to have an average cross section, between 0.0016 and 0.0033 sq. mm., while the cross section, calculated from results obtained by forcing water through, was 0.0025 sq. mm. Again, using a layer of sand, microscopic measurement gave an average cross section of 0.0004 for the interstices while the rate for passage of water gave 0.0002 sq. mm.

Pfeffer[2] gives a too brief account of his results obtained by forcing water through one of his copper ferrocyanide cells under pressures which were varied between 37.8 and 210.2 cm. of mercury. He gives only the pressures and the quotient obtained by dividing the quantity of water which passes per unit of time by the corresponding pressure. This quotient is so nearly constant that it proves the direct proportionality between pressure and amount passing, but as he did not include the temperature, the dimensions of the cell and the volumes of water, one cannot form an idea as to the absolute values, nor institute comparisons with other work.

Sebor[3] made the usual copper ferrocyanide membrane in a Pukall porcelain cup and determined the rate at which water passed through at 18°, varying the pressure from 4 to 23.2 cm. of water. The six observations which he made show the volumes passing to be nearly directly proportional to the pressure, through this narrow range. He made another cell according to Morse's directions[4] and states that this does not permit the passage of water appreciably in 24 hours; but his pressure was low. The rest of his experiments were upon solutions.

[1] Sur les dimensions des intervalles poreux des membranes. Compt. rend., 75, 1809-12 (1872).

[2] "Osmotische Untersuchungen". Leipzig, 70-72 (1877).

[3] Ueber die Diffusionsgeschwindigkeit von Wasser, durch eine halbdurchlässige Membran. Z. Elektrochem., 1904, 347-53.

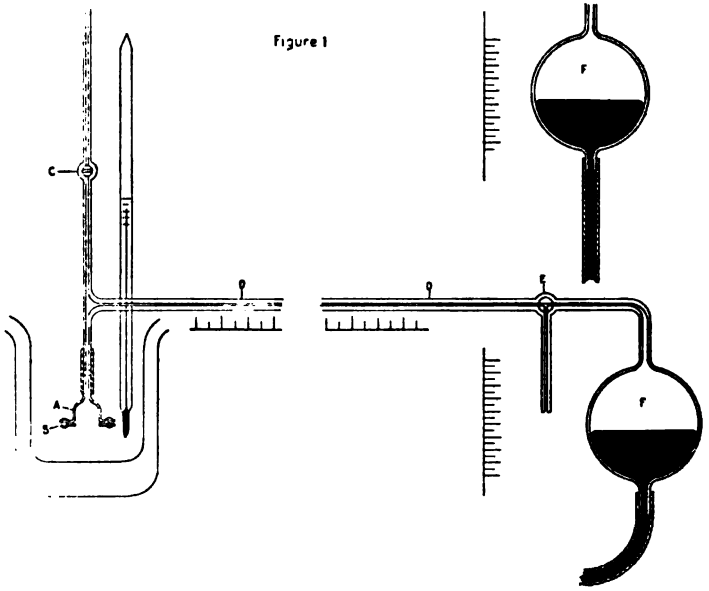
[4] Morse and Horn. Am. Ch. J., 26, 80-86 (1901). Morse and Frazer. Ibid., 28, 1-23 (1902).

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Bechhold[1], in an article which reached the writer just as this communication was about to be sent to the printer, gives a few measurements on the passage of water through acetic-acid collodion and other gelatinized membranes. He touches upon this branch of the subject only long enough to call attention to the desirability of securing exactly the series of measurements, under simplest possible conditions, which are included in my program. His object is to determine what separations, as between emulsions, colloids, and crystalloids and their solvents, can be effected by filtration under pressure through membranes. The holder which he uses for his membranes is similar to mine.

Apparatus.—In a previous article[2] the results of experiments on collodion membranes with pressures between 50 and 250 mm. of mercury, and at temperatures between 1° and 35° were given. Wishing to increase both of these ranges considerably, and also to make direct comparisons between different membrane materials, under conditions as nearly identical as might be, the apparatus shown in Figure 1 was constructed. It is simple yet adequate, and is almost entirely free from a liability to errors due to unperceived leaks.

Figure 1



A flat membrane of the material to be studied closes the 15.0 mm. in diameter opening of the brass holder A and is held in place by the stout ring B, which is drawn up tightly by three screws[3]. The metal bearing on

[1] Loc. cit.
[2] This Journal. November 1907.
[3] In principle this holder is the same as the "osmometer" described by Raoult, Z. physik. Chem., 17, 737 (1895); and Compt. rend., 121, 187.

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the membrane is wide to obviate leaks sidewise. The holder is attached to the vertical glass tube by means of thick rubber tubing of the best quality, wired on and wrapped in sheet copper to prevent stretching when pressure is applied. This joint is eminently satisfactory even under the highest pressures used. D is a capillary tube in which the volumes passing through the membrane are measured. It is placed horizontally in order to avoid the necessity of correcting the pressure for different heights of water[1]. It was calibrated by weighing out with mercury; at 20° one millimeter length contained 7.68 cu. mm. plus or minus 0.08 cu. mm., that is the variations in bore involved an error of about one per cent. and other errors of the method exceeded this. The mercury pressure bulbs F,F. were chosen of good size, 10 cm. in diameter, in order that the small changes in volume, occurring in the course of an experiment, should not materially alter the pressure. The lower bulb was fixed permanently in place, the other was raised and lowered by a pulley and cord. A layer of water on the mercury in the lower bulb eliminated any possible error by evaporation from the meniscus in the capillary. Millimeter scales were placed immediately behind the capillary and between the mercury bulbs. The readings, to the tenth of a millimeter, were made by two cathetometer telescopes at a distance of 1.75 meters from the apparatus. The holder and membrane were immersed in water contained in a beaker which was wrapped in flannel and held in a larger beaker, except when heat was being applied directly. The bulb of a thermometer was in the water close to the membrane. The water was stirred frequently.

Method of Measurement.—Having filled the membrane holder and vertical tube to above the stopcock C, and the capillary nearly to the end of the scale toward the pressure bulbs, with water, the pressure, previously adjusted by raising the movable bulb, was applied by turning the three-way stopcock E. The water was forced through the membrane and the meniscus travelled along the millimeter scale. By means of a stop watch the seconds required for the meniscus to move a given number of millimeters were determined. This interval was usually 10 mm., sometimes it was 50 or 100, occasionally only 2 or 3, depending upon the rapidity with which the water passed out. Sometimes this method was reversed and the number of millimeters traversed by the meniscus in a definite time was measured. The times and distances were selected of such lengths that the errors of observation should be about one per cent.,

[1] Flusin, Compt. rend., 126, 1497 (1898); Ibid., 131, 1308 (1900), Ibid., 132, 1110 (1901) used a horizontal tube in connection with Raoult's "osmometer" in determining rates of osmosis. It may not be superfluous to call attention to the fact that Raoult and he were measuring the rate at which one liquid passed through rubber and other membranes to a different liquid, not the rate at which a mechanical pressure drives a liquid through a membrane bathed by the same liquid on each side. This article is confined to the latter process.

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certainly not more than two per cent. of the values. An interval clock materially aided in measuring the time correctly, for the eye was at the telescope and the position of the meniscus was read when the bell rang. The apparatus as thus set up has a wide range of possible applications.

The Unit for Expressing Results.—The effort was made to approximate, as nearly as possible, to an absolute measure of permeability. The volume passing, and the time, were determined directly; the area of the membrane would be known accurately from the diameter of the orifice in the holder, (15.0 mm.) only the membrane stretches under the influence of the pressure and becomes convex. By lowering the mercury bulb until the pressure is reversed, this convexity is reversed and the contents of this lens of water is forced into the capillary where the volume may be measured accurately. Knowing the diameter and the volume of a lens and assuming a regularity of curvature, the surface area may be calculated This correction, however, has not been applied to the results given in the following tables.

The number of cubic millimeters which pass through one square centimeter of membrane in one minute was adopted as the unit of permeability and this value is denoted by M in the tables and curves[1].

Permeability of Collodion at Different Pressures.—Table 1 contains the results of four series of experiments determining the rates at which water was forced through a collodion membrane by different pressures, the temperatures being maintained nearly constant. The first column contains the pressures in millimeters of mercury, the second the distance through which the meniscus in the horizontal capillary tube travelled in one minute. Three or more separate observations were made and if they agreed fairly well together the average was taken as the final result[2].

[1] The thickness of the membranes, both dry and wet, was measured with a micrometer caliper, before and after experiments, as described in a previous article. The method gives a general idea of relative thicknesses but is not satisfactory, for it does not furnish data to reduce the experimental values to a common unit. Therefore the permeabilities are not "absolute", desirable as it would be to have them so.

[2] As an illustration take the second value in Experiment 6. The following are the laboratory notes from which this was calculated:

Temp.	Level of mercury in upper bulb	Level of mercury in lower bulb	Pressure	Average	Position of meniscus at start	Position of meniscus at end	Time	Seconds for 1 mm.
17°.6	162.3	70.7	91.6		299.0	279.0	7′55″	23.8
	160.7	70.8	89.9	90.6	265.0	255.0	3′44″	22.4
17°.8	160.3	70.6	89.7		252.0	242.0	3′56″	23.6

This was considered a satisfactory agreement and the average value of 2.567 mm. per minute was calculated and inserted in the table. Multiplying this by the factor, obtained by calibrating the capillary, to convert distance into cubic millimeters, and by the factor to reduce the area of the membrane to one square centimeter, gave 11.39 as the value for M, the number of cubic millimeters which passed through one square centimeter in one minute.

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TABLE 1.

COLLODION MEMBRANE NO. 6. PRESSURE VARIED.

Pressure	Mm. per minute	Temperature	M.
Exp. 3[1].			
197.5	5.971	18°.3	26.49
605.8	20.34	18°.3	90.22
Exp. 4.			
204.9	6.717	17°.2	29.80
612.4	19.78	17°.8	87.72
324.0	10.72	18°.0	47.52
Exp. 6.			
60.8	1.793	17°.	7.95
90.6	2.567	17°.7	11.39
132.8	3.637	18°.0	16.14
181.4	4.991	18°.1	22.14
228.2	6.266	18°.4	27.79
320.6	8.956	18°.6	39.72
415.9	11.43	18°.7	50.70
Exp. 7.			
323.6	9.378	19°.9	41.59
415.7	11.94	19°.7	52.97
517.9	14.76	19°.6	65.45

After experiment No. 7 the thickness of the wet membrane was measured. The thinnest portion was in the center, the smallest micrometer reading being 0.065 mm; the thickest portion was at the circumference, close to the holder, the largest reading being 0.105 mm. Five days elapsed between Experiments 3 and 7. The reasonably good agreement shows that subjecting the membrane to considerable changes in pressure produced no material alteration in it. Comparisons between experiments are best made by reference to Figure 2, page 1686, where the results have been plotted, pressures on the abscissa and permeabilities, values for M, on the ordinate. The curves are numbered to correspond with the experiments.

Table 2 contains the results obtained with another collodion membrane. This was cut out of the center of a sheet membrane made by pouring the collodion onto a surface of clean mercury, a method for making them which gave membranes more uniform in thickness than when the collodion was poured onto plate glass. The membrane remained in distilled water for several days before it was used. Numerous measurements of thickness where made on the sheet from which the membrane had been cut; the smallest was 0.235 mm; the largest, 0.265 mm. After the experiments had been completed, the thinnest part of the membrane was found to be 0.065 mm., the thickest part 0.100 mm. Relatively little of the thinning was due to increase in area, for the convexity did not exceed one-tenth

[1] The laboratory note book numbers for the experiments are retained as they give the order in which they were made. The individual values in the tables are also given in the order in which they were obtained.

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the diameter. Apparently the water which it originally contained was squeezed out of it, as if it had been a sponge, and hence the thinning. That this analogy is justifiable was proved by the following simple experiment. A strip of collodion membrane was wiped dry on both sides with a pocket handkerchief and was then pulled and stretched, whereupon there immediately appeared, on both surfaces, a multitude of minute globules of water.

TABLE 2.

COLLODION MEMBRANE NO. 12. PRESSURE VARIED.

Pressure	Mm. per min.	Temperature	M.
Exp. 9.			
115.0	0.587	19°.0	2.602
215.8	1.271	19°.4	5.636
310.6	1.880	19°.4	8.341
412.1	2.646	19°.5	11.73
521.1	4.151	19°.5	18.41
Exp. 10.			
519.4	3.043	19°	13.50
621.7	3.628	19°	16.09
722.6	4.390	19°	19.47
834.3	5.218	19°.2	23.14
527.0	3.273	19°.3	14.52
327.4	2.023	19°.3	8.973
326.3	1.969	19°.3	8.734
113.2	0.7285	19°.3	3.230
Exp. 11.			
117.	0.7052	18°	3.127
306.	1.891	18°.2	8.389
517.3	3.232	18°.2	14.35

Six days elapsed between Exp. 9 and Exp. 11.

It appears safe to conclude from these results:—First, that fairly concordant results can be obtained with this apparatus and method and one membrane; second, that thin collodion membranes immersed in water remain unaltered as regards permeability long enough for repeated experiments; third, that subjecting collodion membranes to the relatively high pressure of 840 mm. of mercury does not materially alter their permeability. This is somewhat surprising, and not in harmony with the picture one has in mind of a capillary structure. It cannot be that they stretch and then gradually come back to their original condition, for the values in Exp. 10 were obtained in the order in which they appear in the table. A slight increase in permeability is noticeable at the lower pressures immediately after the high pressures, but it is too small to show in the curves of Figure 2.

A comparison of the two tables shows that collodion No. 6 was four to six times as permeable as collodion No. 12 under like conditions. Attempts were made to determine the cause of this. It cannot be due to

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difference in thickness, as there was practically none. A number of experiments were carried out with pyroxylin made by nitrating for different lengths of time, ten, twenty, forty and sixty minutes, cotton kindly furnished by Professor A. B. Stevens of the School of Pharmacy. The results were inconclusive and need not be given in detail[1].

Permeability of Gold Beater's Skin under Different Pressures.—Experiments 20 and 21 of Table 3 were carried out with a membrane of gold beater's skin[2]. The maximum thickness of the membrane, dry, before the experiments, was 0.030 mm., the minimum thickness was 0.025 mm; wet, after the experiments, the maximum thickness was 0.040 mm., the minimum 0.020 mm.

TABLE 3.

GOLD BEATER'S SKIN MEMBRANE. PRESSURE VARIED.

Pressure	Mm. per min.	Temperature	M.
Exp. 20.			
209.5	0.535	26°.5-26°.8	2.373
397.0	1.442	26°.9-27°	6.396
599.2	2.670	27°.2	11.84
806.2	4.440	27°.3-27°.5	19.69
207.6	0.765	27°.7	
Exp. 21.			
198.	0.88	25°.5	3.903
102.5	0.36	25°.5	1.597
54.4	0.19	25°.6	0.8428
150.1	0.60	26°.0	2.662
251.0	1.06	26°.1	4.701
351.0	1.44	26°.3	6.387
450.9	1.82	26°.5	8.072
550.7	2.28	26°.5	10.11

The values show a lower permeability than for collodion membranes No. 6 and No. 12, although the latter were between two and three times as thick, and although the temperature was higher during the gold beater's skin experiments.

Permeability of Parchment Paper under Different Pressures.—Parchment paper proved to be the most irregular and vexatious material investigated. While temperature and pressure were held constant, it altered continuously in such a way as to become less and less permeable. The following values for the constant pressure 214 mm. (temperature 26.8°) are given as an illustration. Column 1 gives the time in minutes which

[1] A few qualitative experiments showed that the more completely the solvent alcohol and ether are allowed to evaporate before the membrane is immersed in water, the less permeable is the membrane. As was said in the previous article, Baranetzky (Pogg. Ann., 147, 195-245 (1872)) made the same observation, and the observed differences here are probably due, in the main, to this cause.

[2] Surgeon's Gold Beater's Skin Plaster made by J. Ellwood Lee Co.

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elapsed from the first application of the pressure before the first reading was made. Column 2 gives the seconds required for the meniscus to move one mm. in the capillary. Column 3 gives the seconds which a movement of one mm. should require, calculated on the assumption that a direct proportionality exists between the elapsed time and the diminution in permeability, taking the second value, 16″.6 as the basis for the calculation.

1	2	3
13′.5	7″.9	9″.1
24′.5	16″.6	16″.6
52′.5	33″.8	35″.6
80′	50″	54″.5

What significance this close approximation to a direct proportionality has, is not evident[1].

That this diminished permeability is not due to any permanent change in the membrane, was proved as follows. A pressure of 592 mm. was applied to a membrane until the permeability had fallen to one-half its original value. The pressure was then taken off and the membrane remained for two hours under no pressure. At the end of this time the same pressure was again applied and the membrane showed its original permeability well within the limits of experimental error.

One might imagine that when subjected to a fairly high pressure the membrane would stretch, any capillary holes would increase in diameter, and it would be much more permeable thereafter at all pressures. The diminishing permeability at constant pressure flatly contradicts any such assumption. Moreover, a membrane which showed an initial permeability of 35 was subjected to a pressure of 205 mm. until the permeability had fallen to 5. The pressure was then raised and held at 814 mm. for some time and then reduced to 205 mm. again. Immediately after the reduction the membrane showed a permeability of 12, *i.e.* greater than just before the increase, but only about one-third of the original value.

A satisfactory explanation for the peculiar behavior of parchment paper has not been found. In order to institute some sort of comparison with other membranes, although for the above reasons it is almost void of quantitative significance, Table 4 is given, containing a few, out of a long series of values.

[1] The regularity with which the permeability falls off, and the fact that the falling off is far greater than anything observed with any other material, makes it highly improbable that the phenomenon is due to a mechanical stoppage of pores by solid particles. Indeed there was no indication of a clogging of any membrane by dust, which might be suspended in distilled water, and the preliminary experiments showed that the excessive precautions adopted by other investigators (Schmidt, Baranetzky, Loc. cit.) to remove such particles were superfluous.

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TABLE 4.

PARCHMENT PAPER MEMBRANE. PRESSURE VARIED.

Exp. 17.

Pressure	mm. per min.	Minutes pressure had acted	Temperature	M.
213.9	1.07	92[1]	27°.2	4.745
407.2	5.00	6	27°.3	22.18
595.0	12.76	7	27°.3	56.59
814.5	21.95	5	27°.4	97.34
(205.0	2.10)			

Permeability of Unglazed Porcelain under Different Pressures—A disc was cut from an unglazed porcelain plate and it was given an even surface and thickness by rubbing on fine emery paper. Its maximum thickness was 2.70 mm., its minimum thickness 2.64 mm. It was put in the membrane holder with washers of dental rubber dam on each side[2].

Table 5 gives the values obtained. Plotted on the diagram Exp. 16 gives the rapidly ascending curve 16. In order to show the full course of the experiments within the limits of the figure, the values for M. were divided by four and curves (15) and (16) were obtained.

TABLE 5.

PORCELAIN MEMBRANE. PRESSURE VARIED.

Exp. 15.

Pressure	Mm. per min.	Temperature	M.
234.0	25.86	21°.8	114.7
126.0	15.46	21°.8	68.58
71.5	9.50	21°.8	42.14
313.	41.39	21°.9	183.5
123.3	17.14	21.°9	76.03

Exp. 16.

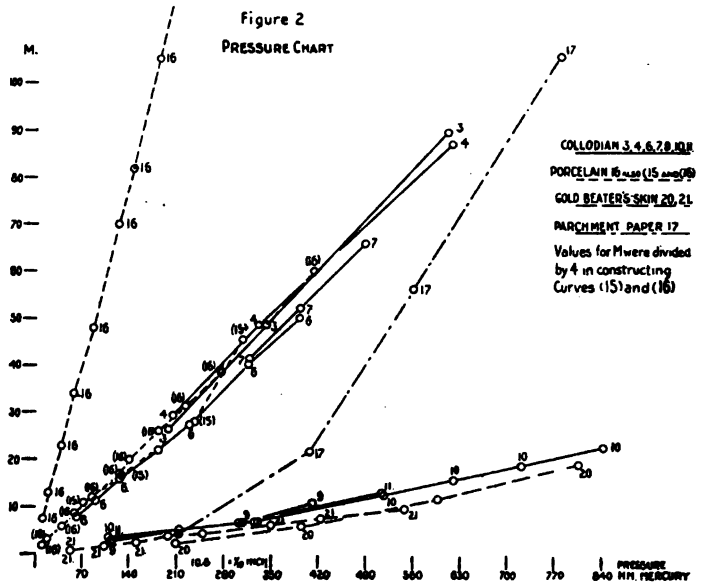
412.	54.55	21°.7	241.9
333.	42.86	21°.8	190.1
277.5	35.30	21°.9	156.5
227.2	28.77	22°.2	127.6
185.2	23.69	22°.4	105.1
145.2	18.52	22°.6	82.15
122.5	15.79	22°.7	70.03
85.3	10.77	21°.9	47.80
58.8	7.68	22°.1	34.06
38.1	5.11	22°.2	22.65
18.7	2.90	22°.3	12.85
9.8	1.70	22°.5	7.50

[1] These values have the following significance: The pressure of 213.9 mm. had been on the membrane for 92 minutes before the recorded observation was made; the pressure was raised to 407.2 mm. and after this new pressure had been on for 6 min. the first reading was made for that observation, and so on.

[2] Water could escape out of the rim of this disc, but the shortest distance from the inner surface in contact with the water under pressure, to the rim, was more than 6 mm. This sidewise leak could not alter the general trend of the results, although it would have to be stopped to obtain accurate values for the absolute permeability.

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All the results with different pressures are brought together in Figure 2. Pressures are laid off on the abscissa and values for M on the ordinate.



Poiseuille's formula[1] for the passage of liquids through capillary tubes is

$$Q = k \frac{PD^4}{L} T$$

where Q = the quantity of liquid passing in time T, P = the pressure, D = the diameter, L = the length of the capillary and k = a constant for a definite temperature. According to this formula the quantities which pass in unit time are directly proportional to the pressure. If the passage of water through the membranes investigated be a capillary phenomenon, the curves in Figure 2 should be straight lines. They are straight lines, within the limits of experimental error, therefore the passage of water through these membranes is probably a capillary phenomenon. If they had not been straight lines, that might have been accepted as conclusive proof that the phenomenon was not capillary, but the converse does not hold, and, although they are straight lines, this does not definitely prove that the phenomenon is capillary. Still, it is fairly strong evidence in favor of that view.

Permeability of Collodion at Different Temperatures.—The following tables show the change in permeability of membranes with changes of temperature, pressure being held nearly constant. Table 6 gives the values obtained with collodion membrane No. 6 the same used in experi-

[1] See any text on physics, for instance Chwolson. Lehrbuch der Physik, Vol. 1, p. 959 (1902).

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ments 3, 4, 6, and 7, and Table 7 gives the values obtained with collodion membrane No. 12, used also in experiments 9, 10 and 11.

Poiseuille's formula to express the variation of k with the temperature is: $k = k_0(1 + 0.03368t + 0.000221t^2)$[1]

In my experiments M = Q, P and T were held constant. If we assume that D and L remained constant, $\frac{PD^4}{L}T$ = a constant, C, and we have, $M = kC$. Substituting in the temperature equation we have $\frac{M}{1 + 0.03368t + 0.000221t^2} = k_0C$, or we can calculate the value of k_0C from the measured M and temperature. If the laws for the flow of liquids through capillary tubes apply, we should get always the same value for k_0C throughout one experiment. Of course these values will not remain the same in different experiments, if the pressure is altered, nor if different membranes are used, when doubtless D and L have different values.

These values for k_0C were calculated as described for three collodion experiments and for the porcelain plate experiment and the results of the calculations are included in the tables in the columns headed k_0C.

TABLE 6.

COLLODION MEMBRANE NO. 6. TEMPERATURE VARIED.

Exp. 5.

Pressure	Mm. per min.	Temperature	M	k_0C
324.2	25.54	72°.	113.2	24.80
323.9	22.87	68°.7	101.4	23.27
323.6	21.63	65°.5	95.92	23.09
323.3	20.87	62°.0	92.58	23.51
323.0	19.52	56°.0	86.56	24.18
322.7	18.75	54°.1	83.18	23.98
322.4	17.78	51°.2	78.86	23.88
321.4	15.39	42°.4	68.25	24.16
321.3	12.35	33°.0	54.79	23.29
321.2	10.31	24°.0	45.76	23.64

TABLE 7.

COLLODION MEMBRANE NO. 12. TEMPERATURE VARIED.

Exp. 12.

305.	1.091	0°.9	4.840	4.697
300.8	1.120	2°.6	4.967	4.561
301.0	1.282	7°.0	5.689	4.564
299.1	1.592	14°.5	7.058	4.598
298.0	1.695	17°.9	7.518	4.492
298.2	1.783	19°.5	7.909	4.543
297.7	1.997	24°.5	8.857	4.524
297.5	2.355	30°.0	10.44	4.726
297.8	2.816	38°.5	12.48	4.755

Exp. 13.

320.0	2.006	20°.0	8.898	5.050
319.7	2.786	32°.5	12.36	5.308
318.8	3.215	44°.0	14.26	4.901
318.7	4.146	56°.2	18.39	5.121
318.7	5.081	68°.5	22.53	5.186
319.1	6.546	85°.5	29.03	5.282
317.1	6.384	99.°2[2]	28.31	4.345

[1] See Chwolson p. 659.

[2] The water was boiling vigorously; the barometric pressure was 738.6 mm.

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At temperatures above 80° the movements of the meniscus became rather irregular and concordant results were hard to obtain. Apparently a maximum permeability is reached at about this temperature, and a slight diminution occurs upon further heating. This behavior was totally unexpected. The value of 29.03 is the average from eleven and the value 28.131 is the average from ten separate observations.

Observations made the day after Experiment 13, proved that the permeability of the membrane at low temperatures had not been altered by the boiling.

There is a fairly good agreement between Experiments 12 and 13. This is best seen by reference to Figure 3, where all the results with different temperatures are brought together in the form of curves, temperatures being laid off on the abscissa and values for M. on the ordinate.

The permeability of collodion membrane No. 6 increases much more rapidly with increase of temperature than does that of collodion membrane No. 12. But the coefficient of the increase is about the same; roughly speaking, an increase of 30° to 35° about doubles the rate at which water passes.

Permeability of Parchment Paper at Different Temperatures.—Parchment paper membranes were even more troublesome in the temperature experiments than in the pressure experiments. As the temperature was increased the permeability at first fell off, reached a minimum and then rose. The falling off of the permeability of parchment with time is not the sole cause of this erratic behavior. Observations were made at definite time intervals and it was very evident that the heating itself caused a diminution in the permeability. The numerical values which demonstrated this fact will be omitted, to save space. They were used to plot Curve 19 of Figure 3.

Permeability of Gold Beater's Skin at Different Temperatures.—Owing to a series of difficulties and accidents, having little or nothing to do with the principles involved, concordant results upon the influence of temperature on the permeability of gold beater's skin membranes have not as yet been obtained.

Permeability of Porcelain at Different Temperatures.—Table 9 shows the change in permeability with temperature, of the same porcelain disc used in Experiment 15.

TABLE 9.

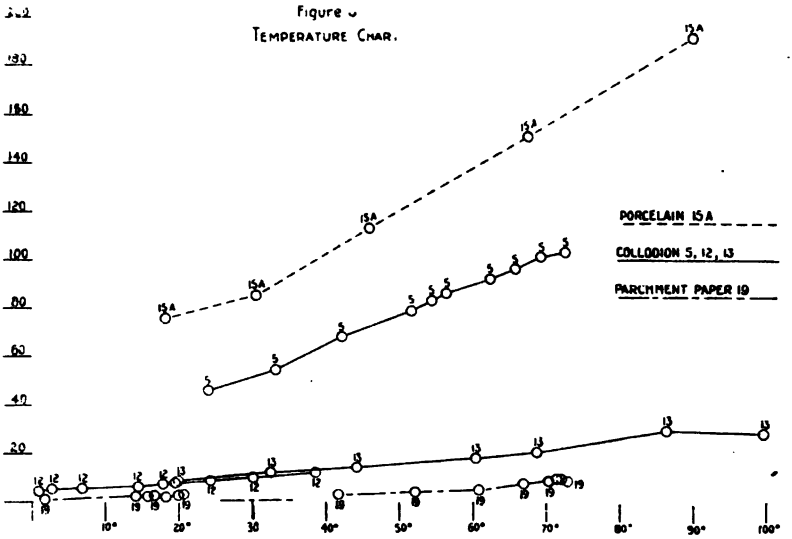
PORCELAIN MEMBRANE. TEMPERATURE VARIED.

Exp. 15 A.

Pressure	Mm. per min.	Temperature	M.	k_0 C
123.3	17.14	21°.9	76.03	41.13
123.5	20.00	30°.5	88.72	39.73
122.6	25.71	45°.5	114.0	38.13
122.4	34.01	67°.2	150.9	35.41
119.0	43.25	89°.3	191.8	33.24

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The results obtained by varying the temperature are brought together in the form of curves in Figure 3. Temperatures are laid off on the abscissa and values for M on the ordinate.



The resemblance between the curves in this figure is not so striking as it was between the curves obtained for varying pressures, and yet, if we disregard the peculiarities shown by parchment paper they are enough alike to furnish further evidence that the nature of the process, whatever it may be, is the same with each of these membranes.

The values for k_0C are nearly constant in each series with collodion membranes. This constancy means that the rate of passage of water through these membranes is expressible by the capillary laws. The lack of constancy of k_0C for the porcelain plate, precisely the case in which one would expect the best agreement, is probably because some of the necessary conditions discovered by Poiseuille were not fulfilled, for instance, the "capillary tubes" in the porcelain plate may have been below the minimum length for their diameters.

Discussion of Results and Theory.[1]

All the theories regarding the function of the membrane in osmotic

[1] Anything like a bibliography of the theories regarding osmotic phenomena would be too extensive for insertion here. Besides those to whom reference is made in the text, it would have to include such well known names as Arrhenius, Batelli and Stephanini, Lord Berkeley, Dutrochet Findlay, Fischer, Griffiths, Hamburger, van't Hoff, Hulett Jolly, Kahlenberg, Larmor, Liebig, Lowry, Ludwig, Magnus, Morse and his fellowworkers, Nernst, Nollet, Ostwald, Parrot, Pickering, Poisson, Poynting, Quincke, Ramsay, Raoult, Tammann, J. Traube, M. Traube, De Vries, Walden and many others. I have therefore reduced my citations to the lowest possible number, and desiring to recognize priority so far as my knowledge of the literature permits, have given preference to the earliest articles known to me in which the appropriate statements may be found.

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cells may be ranged along a scale at one end of which is the purely physical conception of capillary pores of measurable diameters, at the other, the purely chemical conception of chemical combination between the membrane itself and the substance passing through it. Each extreme and many intermediate hypotheses, found expression much earlier than appears to be generally realized. The two extreme views were, and still are, held to be mutually exclusive. For instance, Fick[1] said that we must distinguish between "pore diffusion" occurring through capillary openings, and true endosmosis, occurring through the much smaller molecular spaces. He concludes, with regret, that since the capillary theory, as so ingeniously worked out by Brücke[2], does not agree with all the facts it must be materially modified or supplanted by something else. He says he sees no alternative but "to adopt the very vague idea that osmotic processes do not occur through so called pores but rather through the actual molecular interstices".

This is, in effect, the "solution theory", the main premise of which is that a substance will pass through a membrane only if soluble in that membrane. This theory probably has more supporters today than any other. It is by no means new, for one could hardly read Graham's or Liebig's articles, particularly the latter's in which he describes his determinations of the "imbibition" of liquids by membranes, without feeling that they had this solution idea in mind. But Lhermite[3] was the first to state the "solution theory" clearly and to support it with good experimental evidence. To him we owe the ingenious "three liquid layers" experiments which have since been repeated by numerous others with various modifications. With the express intention of demonstrating that a substance which passes through a membrane dissolves in that membrane, he superposed layers of water, castor oil and alcohol, also of water, turpentine or essence of lemon and dilute alcohol, also layers of oil of bitter almonds, water and ether, in cylinders. In each case he found the uppermost layer dissolved in the middle layer and passed through this to the bottom layer. Although references to his article are given, in some way he does not seem to have received the full credit he deserves. That his priority with the solution theory is beyond question, is conclusively proved by the following quotations from the article already cited. On page 427 he says: "Cette expérience fait parfaitement comprendre le jeu de la membrane. Quel que soit le nom qu'on donne à la faculté qu'elle a de s'impregner de certains liquides et de les partager avec d'autres liquides qui ont pour les premiers autant d'affinité qu'elle, les conséquences de cette propriété doivent être les mêmes que celles qui

[1] Ueber Diffusion. Pogg. Ann., 94, 59-86 (1855).

[2] Beiträge zur Lehre von der Diffusion, tropfbarflüssiger Körper durch poröse Scheidewände. Pogg. Ann., 58, 77-94 (1843).

[3] Recherches sur l'Endosmose. Ann. chim. phys., [3], 43, 420-431 (1855).

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résultent de la faculté dissolvante". Again on page 431 he says: "En résumé, les phénomènes d'endosmose ne sont qu'un cas particulier de la force dissolvante. La propriété des tissus de s'imbiber de liquide est le contre-pied de la solubilité d'un solide dans l'eau. La cloison membraneuse peut être considérée comme un troisième liquide". Nothing could be clearer than that fifty-two years ago Lhermite said a substance passing through a membrane dissolved in that membrane.

One more instance may be given to establish the fact that these views were at the basis of much work and that they were considered as contradictory. Eckhard[1], as a result of extensive investigations reached the conclusion that there was not experimental evidence enough to prove the necessity of distinguishing between two kinds of permeabilities, one through capillaries and the other through molecular interstices, and that the capillary theory is capable of covering all cases. Eckhard's conclusion is also open to an interpretation the converse of his own, namely, that the "molecular interstice theory" is capable of covering all cases, even those undoubtedly capillary.

As a matter of fact the different views, even the two extremes are not mutually contradictory but may be entertained simultaneously. They may be unified as follows. The experimental results given in this article demonstrate that the laws which have been found for the passage of liquids through capillary tubes apply to the passage of water through the membranes studied. These membranes may be considered as typical of certain classes, parchment paper and collodion of vegetable membranes, gold beater's skin of animal, and a porcelain plate of inorganic membranes. Capillary pores are without doubt present in a porcelain plate; good authority has been cited in favor of the view that water passing through a collodion membrane dissolves in that membrane, *i. e.*, occupies intermolecular spaces; but the continuity in the nature of the phenomenon through all these membranes is unmistakable. Pfeffer's[2] results also indicate that the capillary laws apply to the passage of water through copper ferrocyanide membranes and Schmidt's[3] results indicate the same for animal membranes, therefore we are justified in saying that *the rate of passage of liquids through molecular interstices is expressible by the same laws which formulate the rate of passage of liquids through capillary tubes.*

This statement not only harmonizes theories at present in conflict but has some interesting corollaries, for it furnishes a link connecting capillary with chemical processes. We have no alternative but to assume that a solute occupies molecular interstices of the solvent, then the phenomena

[1] Der gegenwärtige experimentelle Thatbestand der Lehre von der Hydrodiffusion durch thierische Membranen. Pogg. Ann., 128, 61-100 (1866).

[2] Loc. cit.

[3] Ibid.

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of solution and diffusion must be in the same general class with capillary phenomena. The interesting work now being done upon the theory of of "hydrates in solution" makes it increasingly probable that there is no sharp demarkation between the process of solution and chemical combination. Such continuity and lack of bqundary lines is a well recognized universal principle in natural phenomena. Thus the phenomena of chemical affinity seem to merge, without any abrupt change, into capillary phenomena. It is then probable that facts obtained by the study of the diffusion of liquids through membranes will increase our knowledge of chemical processes.

This idea that capillary phenomena are different in degree but not in kind from chemical phenomena has been neglected, or forgotten perhaps, but is not new. To refer once more to that brief but extraordinary article by Lhermite,—on page 421 he says: "I hope to demonstrate by my own experiments and by a discussion of those of my predecessors, that osmosis, or endosmosis, is not the result of a special force, but of affinity itself, extending the acceptation of this word to include capillary attraction, which is the first manifestation of affinity and which we might call tendency toward affinity". In order that there may be no possibility of misunderstanding his meaning, on page 424, he says: "I said above that we might consider capillary force as the first degree of chemical affinity".

Summary.

1. An apparatus is described to determine the permeabilities of equal areas of membranes through wide ranges of pressure and temperature both accurately and quickly.

2. The permeabilities for water of collodion, parchment paper, gold beater's skin, and unglazed porcelain membranes were determined in terms which, while not quite deserving the name of specific or absolute permeabilities, approximate this desideratum.

3. These results made possible comparisons between the relative permeabilites of the substances studied.

4. The change in permeabilities with change in pressure and with change in temperature was determined through a rather wide range.

5. The fact that Poiseuille's laws for the passage of liquids through capillary tubes apply to the passage of water through the four membranes, was demonstrated graphically and by calculation.

6. The conclusion was reached that the rate of passage of liquids through molecular interstices is expressible by the same laws which formulate the rate of passage of liquids through capillary tubes.

UNIVERSITY OF MICHIGAN,
September, 1907.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF THE LELAND STANFORD JUNIOR UNIVERSITY.]

POTASSIUM AMMONOSTANNATE.

By F. F. FITZGERALD.

Received October, 15, 1907.

In former articles[1] in this Journal experiments were described which were undertaken with the object of preparing an ammonia analogue of the potassium zincate which is formed by the action of an excess of potassium hydroxide upon metallic zinc, zinc oxide or zinc hydroxide. The result of these experiments led to the present attempt to prepare other representatives of the same general class. Applying the method used successfully by Franklin in preparing pure potassium ammonozincate to a preliminary examination of the behavior of a number of metallic salts it was found that among them stannic iodide gave the most promise of success.

As is well known, stannic hydroxide is first precipitated when potassium hydroxide is added to an aqueous solution of a stannic salt to be followed, upon the addition of an excess of the precipitant, by the conversion of the stannic hydroxide into potassium stannate. If the analogous reaction takes place in ammonia, potassium amide should first cause a precipitation of stannic amide, imide or nitride, from a solution of a salt of tin in liquid ammonia, which precipitate should then, by the action of an excess of potassium amide, be changed into a potassium ammonostannate. That such a reaction takes place was found to be the case. The analogy between the reactions in the two solvents is expressed by equations such as the following :

$$SnI_4 + 4KOH = Sn(OH)_4 + 4KI$$
$$Sn(OH)_4 + 4KOH = Sn(OK)_4 + 4H_2O$$
$$SnI_4 + 4KNH_2 = Sn(NH_2)_4 + 4KI$$
$$Sn(NH_2)_4 + 4KNH_2 = Sn(NHK)_4 + 4NH_3.$$

Preparation of Potassium Ammonostannate.—The preparation of the pure compound was effected by the action of an excess of potassium amide upon absolutely water-free stannic iodide in accordance with the equation,

$$SnI_4 + 6KNH_2 = Sn(NK)_2.4NH_3 + 4KI.$$

The preparation of the potassium amide used in these experiments and the general mode of manipulation followed, are the same as described by Franklin in a former article[2]. In a number of preliminary experiments the stannic iodide used was from a specimen by Kahlbaum. Analyses of preparations made from this sample, although they approximated a definite compound, gave indications of the presence of some impurity,

[1] Fitzgerald: This Journal, 29, 657. Franklin: Ibid., 29, 1274.

[2] This Journal, 27, 830.

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presumably oxygen introduced as water with the stannic iodide. To avoid any possible contamination by water or other impurity, the following procedure was followed. Stannic iodide was prepared by heating a mixture of iodine and excess of metallic tin in a retort and distilling the stannic iodide thus formed, avoiding at the same time any unnecessary exposure to the air. The stannic iodide thus obtained, together with a small quantity of metallic tin was introduced through the tubulure, A, into the leg, B, of a piece of apparatus blown as represented in Figure 1.

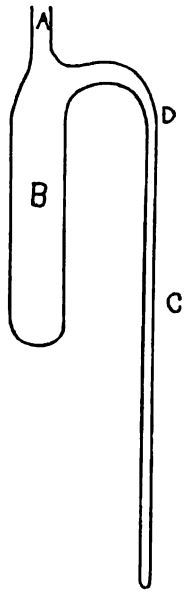


Fig. 1.

The tubulure was softened before the blowpipe, thickened and drawn down to a small diameter preliminary to sealing. The apparatus was then connected to an air pump and completely evacuated, after which the tube was sealed off at the thickened portion. By a judicious application of heat, the salt was then distilled into the leg, C, giving thus, a specimen of pure anhydrous stannic iodide since any stannous iodide or basic salt must remain behind in the leg, B. The tube, C, was then cut off at D, and its contents preserved by placing a cap over the open end of the tube. The procedure for the introduction of this stannic iodide into the reaction tube was identical with that followed for introducing pure, dry potassium.[1] When liquid ammonia is distilled into the leg containing

[1] On looking up Franklin's description ot this procedure, (This Journal, 27, 831), the writer finds that the details are omitted. All but absolute exclusion of moisture from the reaction tube is assured by the following simple procedure. With the leg, B, Fig. 2, closed by means of a stopper and a current of ammonia gas escaping at A, the open end of the tube containing the stannic iodide is held in the escaping

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the stannic iodide, the salt dissolves to a dense, colorless solution. Ammonolysis of this solution of stannic iodide is shown by the following procedure. Just sufficient ammonia is distilled into the preparation tube to dissolve the stannic iodide, solution being facilitated by shaking the tube. Then as more ammonia is distilled into the tube in such a manner as not to mix the contents, the separation of a white precipitate is observed between the layer of the concentrated solution of stannic iodide and the freshly distilled ammonia. On shaking the tube the precipitate disappears. The separation of the precipitate may be observed several times by repeating the operations above described. After a relatively large amount of liquid has been added, the precipitate becomes permanent and the separation of the tin from the solution is complete, as is shown by the fact that addition of potassium amide to the supernatant solution fails to produce any further precipitation. The addition of ammonium iodide, which, it may be remarked, acts as an acid in ammonia solution, prevents the ammonolysis of the tin salt.

On pouring a solution of potassium amide into a solution of stannic iodide a voluminous, white, precipitate of variable composition is thrown down. Analysis of this precipitate shows it to contain tin, iodine and nitrogen but not in such proportions as to indicate the formation of a definite com-

gas at A, while a small cylinder is cut from the tube of stannic iodide and rejected, thus removing the small quantity of stannic iodide contaminated by previous exposure to the air. The tube containing the stannic iodide is then introduced into the opening at A, and a cylinder of such length as desired is cut off and pushed into this leg to a distance sufficient to permit the sealing of the latter before the blow-pipe. Before proceeding

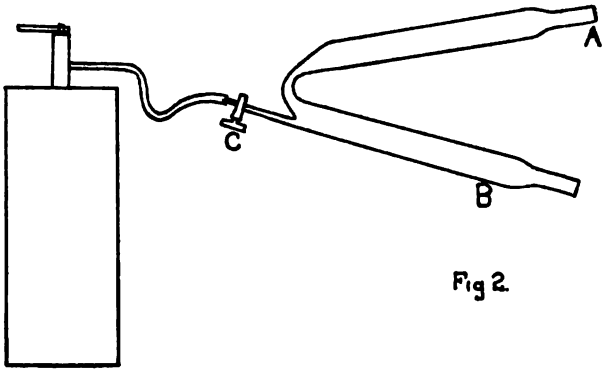


Fig 2.

to seal this leg of the reaction tube, the opening, A, is closed by means of a stopper while the leg, B, is simultaneously opened for the escape of the current of ammonia, thus excluding any possibility of accession of moisture through A during the operation of sealing. The introduction of metallic potassium into leg, B, is accomplished in the same manner, B being closed, and the stopcock plug, C, removed during the sealing of this second leg.

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pound. It is therefore to be looked upon as a mixture of ammonobasic salts of tin. Addition of potassium amide in excess, changes this flocculent precipitate into a sharply crystalline product. If just sufficient potassium amide is introduced to bring about the reaction, (which can be determined by the fact that the smallest excess of the amide changes the color of the solution to a slight yellow), larger crystals are obtained than is the case when a large excess is added. The crystals of the tin salt differ in several particulars from those of the analogous zinc salt. They are formed in a few seconds after the addition of an excess of potassium amide while the zinc salt is not entirely crystalline until after the lapse of hours or days. The crystals are also much smaller than those of the zinc salt and reflect the light very beautifully while the zinc salt crystals are apparently much less dense optically.

The preparations were washed and prepared for analysis in the manner previously described.[1]

For analysis the substance was dissolved in dilute hydrochloric acid and divided into aliquot parts. In one portion the nitrogen was determined by distillation with potassium hydroxide and titration with standard acid solution. From another portion the tin was precipitated as sulphide, ignited and weighed as the oxide. The potassium contained in the filtrate from the stannic sulphide was weighed as the sulphate.

Three separate preparations gave the following results:

(I). One fourth of 0.4803 g. of substance gave 0.0344 g. nitrogen, the remaining three fourths gave 0.1861 g. stannic oxide and 0.2125 g. potassium sulphate. (II). One fourth of 0.4591 g. of the substance gave 0.0326 g. nitrogen, and 0.0592 g. stannic oxide. (III). One eighth of 1.6859 g. of the substance gave 0.0602 g. nitrogen. Three eighths of 1.6859 g. of the substance gave 0.3261 g. stannic oxide and 0.3770 g. potassium sulphate.

	Calculated for $Sn(NK)_2.4NH_3$	Found		
		I	II	III
N	28.65	28.65	28.40	28.58
Sn	40.57	40.65	40.64	40.65
K	26.70	26.50		26.80

Properties of the Salt.—Potassium ammonostannate is but slightly soluble in liquid ammonia but dissolves readily in a liquid ammonia solution of ammonium iodide[2]. It is also readily soluble in aqueous hydrochloric acid, the action being violent and accompanied by the evolution of much heat. It is not explosive, but if heated in contact with the air it decomposes violently and with incandescence, the heat evolved being

[1] Franklin: This Journal, 27, 830.

[2] This salt as Franklin (This Journal, 27, 822.) has pointed out acts as an acid in liquid ammonia so that the explanation of its action in this case is given by the equation, $Sn(NK)_2 + 6NH_4I \rightleftharpoons SnI_4 + 8NH_3 + 2KI$.

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due to the oxidation of the tin and potassium. When heated *in vacuo* potassium ammonostannate remains unaffected up to 60°. As the temperature is increased above this point it loses ammonia.

The Compounds, $Sn(NK)_2.NH_3$ and $Sn(NK)_2.\frac{1}{2}NH_3$(?)—A specimen of potassium ammonostannate with four molecules of ammonia of crystallization was heated *in vacuo* to a maximum temperature of 145° until the evolution of ammonia ceased. 0.3578 g. of the substance lost 0.0623 g. of ammonia or 17.4 per cent. of its weight. The amount of nitrogen in the residue was found to be 0.502 g. or 17.0 per cent. The calculated loss of weight for the expulsion of three molecules of ammonia is 17.4 per cent. while the calculated content of nitrogen in the salt with one molecule of ammonia is 17.3 per cent. It therefore appears that the red residue formed by heating the compound, $Sn(NK)_2.4NH_3$, to 145° is to be assigned the formula, $Sn(NK)_2.NH_3$ or possibly $NH:Sn:(NHK)_2$.

A second specimen weighing 0.4356 g. was heated gradually up to 145°, at which temperature the evolution of ammonia ceased. The volume of ammonia given off was calculated to weigh 0.0768 g., which corresponds to 17.6 per cent., thus confirming the results of the experiment described above. As the temperature was raised to 175° an additional quantity of ammonia was given off, but even heating for hours at 316° was found insufficient to drive off all the ammonia. The final product approximated in composition the formula, $Sn(NK)_2.\frac{1}{2}NH_3$, as is shown by the following analytical data. The total loss of ammonia from 0.4356 g. of the original substance was 0.0835 g., corresponding to 19.0 per cent. The calculated loss for three and one-half molecules is 20.3 per cent. In the residue 0.0542 g. of nitrogen was found, corresponding to 12.4 per cent. while the amount calculated for the compound with half a molecule of ammonia is 11.9 per cent. The existence of a compound $Sn(NK)_2.\frac{1}{2}NH_3$. requires confirmation.

The final product obtained by heating the original compound is a brick red powder which remains unfused at a temperature of 316°. On allowing water to enter the tube, but in such a manner that the liquid does not come in contact with the substance, the latter is rapidly acted upon by the water vapor and is changed into a white mass which dissolves readily and completely in aqueous hydrochloric acid. When liquid water was allowed to come into contact with the red powder, violent action followed, resulting in the deposition of a metallic mirror on walls of the tube and the separation of a quantity of gas. The metallic mirror dissolved in hydrochloric acid with the evolution of gas and consequently must have been metallic tin. The gases formed during the decomposition of the salt were not identified, but it is not obvious how the separation of tin and gas by the action of water is to be explained other than by the assump-

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tion that a portion of the salt was decomposed in accordance with the equation,

$$Sn(NK)_2 + 2H_2O = Sn + N_2 + H_2 + 2KOH.$$

This partial decomposition is to be ascribed to the violence of the action of liquid water and the high temperature thereby produced. The hydrolytic action of the water vapor is to be represented by the equation,

$$Sn(NK)_2 + 6H_2O = Sn(OH)_4 + 2KOH + 2NH_3.$$

Summary of Results.

It is shown by the work described above that a potassium ammonostannate of the formula, $Sn(NK)_2.4NH_3$, $(NH_2)_2:Sn:(NHK)_2.2NH_3$, $(KHN)_2:Sn:(NHNH_4)_2$, or $Sn(NH_2)_4.2KNH_2$, an ammonia analogue of potassium stannate, is formed when a solution in liquid ammonia of potassium amide in excess is allowed to act upon stannic iodide, likewise in solution in liquid ammonia, and that this compound, when heated to a temperature not in excess of 145°, loses three molecules of ammonia of crystallization to form the compound, $Sn(NK)_2.NH_3$ or $HN:Sn:(NHK)_2$. From this compound even by heating for several hours *in vacuo* to 316° it was not possible to obtain the ammonia-free salt.

The writer is under obligations to Dr. E. C. Franklin of Stanford University for his many suggestions and great assistance in carrying on this investigation.

STANFORD UNIVERSITY,
California, *Summer* 1907.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

THE SPECIFIC RADIOACTIVITY OF URANIUM.[1]

BY HERBERT N. MCCOY AND W. H. ROSS.

Received October 14, 1907.

It may be considered as fully established[2] that the specific activity of Uranium in any pure uranium compound or in any uranium mineral, free from thorium, is in either case strictly constant. The value of these constants has been given as 790 for pure compounds and 3280 for minerals. These values were obtained from activity measurements made with a distance of 3.5 to 4.5 cm. between the active film and the charged electrode of the gold leaf system. It is now known[3] that the ranges of RaA and RaC both exceed 4.5 cm.; for which reason the value given for the specific activity of uranium in a mineral is too low. New measurements have now been made by means of a new improved gold-leaf electroscope which has an ionization chamber 19.5 cm. square and allows a distance of 8.5 cm. between the active films and the superimposed

[1] Read, in abstract, before the Amer. Phys. Soc., Chicago, Dec. 1, 1906; Phys. Rev., Jan., 1907.

[2] McCoy, Ber., 37, 2641 (1904); This Journal, 27, 391 (1905); Phil. Mag., 11, 176 (1906); Goettsch, This Journal, 28, 1541 (1906).

[3] Bragg and Kleeman, Phil. Mag., 10, 318 (1905).

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electrode. The scale of the micrometer microscope, used to read the position of the gold-leaf, corresponded to potentials between 400 and 480 volts. With this new electroscope the activity of a pure uranium compound was the same at 4.5 cm. as at 8.5 cm. from the electrode. But a thin film of a uranium mineral was about 4 per cent. more active at 8.5 cm. than at 4.5 cm.

The recent work on the range of the α rays has also served to indicate another possible error in the method previously employed for the measurement of activity. According to this method films of the active material were deposited in flat, circular, metal dishes about 7 cm. in diameter, with rims 0.8 cm. high.[1] Inasmuch as the solid angle subtended by the rim, with any point of the film as center, was the same for all films, the rims being of equal height, it was thought, at first, that the same fraction of the radiation would be cut off by the rim in all cases. However, films sending out α-rays with greatest effective range should suffer greatest proportionate loss of activity on account of the rims. Experiment confirmed this supposition, although the difference in percentage loss was not great. Thus, while the actual diminution of the activity due to the rims was found to be 8.2 per cent for uranium oxide, the corresponding decrease in the case of uranium minerals amounted to 8.8 per cent.; a difference of 0.6 per cent. For the new measurements all films were deposited on perfectly flat surfaces. This was readily done by placing false bottoms, 7.00 cm. in diameter, made of sheet copper, in the tin vessels previously used. After the deposition of the film by the sedimentation process[2] upon the false bottom, the latter was removed from the tin vessel. Perfectly satisfactory films, weighing as little as one milligram per sq. cm., were easily made in this way.

The standard of activity was a thick film of the oxide U_3O_8, weighing about 0.025 g. per sq. cm. It was deposited on a flat copper plate 7.00 cm. in diameter. The activity due to each sq. cm. of such a film is taken as the unit of activity. The total activity of 1 g. of any substance, in terms of such a unit, may be called its specific activity.

The specific activity of pure uranium oxide, U_3O_8, was redetermined from measurements of a series of new films on flat plates, the new electroscope being used with the films at 8.5 cm. from the electrode. The results, calculated by the method of graphical extrapolation previously used[3] gave for the specific activity of the oxide, 676. Since the oxide contains 84.85 per cent. of uranium, the specific activity of uranium is 796. This value differs but little from the value, 790, found earlier.

For the new experiments upon minerals, new samples were made from

[1] Tin-plate jelly-glass covers were used.

[2] McCoy, This Journal, 27, 395 (1905).

[3] Phil. Mag., 11, 176 (1906).

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the three lots of pitchblende previously studied. In the analysis the uranium was separated essentially by Boltwood's modification[1] of Brearley's method. The uranium phosphate so obtained was ignited and weighed. The pyrophosphate was then dissolved in dilute sulphuric acid, reduced with zinc and titrated with permanganate. The volumetric results agreed with the gravimetric very closely. Duplicate or triplicate analyses were made of each sample. All of the samples were analyzed for thorium by Neish's method[2], 5 gram portions of each mineral being taken, but no trace of thorium was found in any case.

TABLE I.

		Locality.	Per cent. of Uranium.	Specific Activity, k_1
1.	Pitchblende	Unknown	44.7	1582
2.	"	Central City, Colorado	54.0	1908
3.	"	Gilpin Co., "	58.1	2018

In order to obtain exact results, the specific activities given above must be corrected for the activity of the emanation spontaneously lost; for, as Boltwood has shown[3] all minerals give off a portion of their emanation when powdered. The amount of emanation spontaneously lost was determined essentially in the manner described by Boltwood, the emanation being allowed to accumulate in maximum amount. The emanation was removed from the tube containing the known weight of powdered mineral, by drawing through the former about 250 cc. of air. This was collected in a flask and allowed to stand fifteen minutes before being conducted into the exhausted electroscope. The activity was measured after the emanation had remained in the electroscope two hours, at the end of which time the activity had become practically constant.

In the determination of the emanation retained in a powdered mineral, we have found it possible to substitute for the complicated apparatus and procedure employed by Boltwood, a very simple method. An accurately weighed portion of the mineral, about 0.03 g., was placed in a 150 cc. flask fitted with a rubber stopper and bent glass tube. The latter was connected by a rubber tube to another bent glass tube which just passed through the stopper of a liter flask filled with dilute sodium hydroxide solution. A second tube passed through the stopper of the liter flask and formed a siphon leading from the bottom of the flask emptying into a large beaker containing a little water. The process consisted in pouring onto the mineral in the smaller flask a mixture of 15 cc. of dilute sul-

[1] Phil. Mag., 9, 603. We found it necessary to alter the proportions of the reagents suggested by Boltwood. The details of our procedure are given elsewhere. W. H. Ross, Thesis, Univ. Chicago, 1907.

[2] This Journal, 26, 780 (1904). We have thoroughly tested Neish's method in connection with studies on thorium minerals and found it remarkably accurate.

[3] Loc. cit.

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phuric and 5 cc. of nitric acids, inserting the stopper and boiling gently for 10 to 15 minutes. The air originally in the small flask and the gases formed by the reaction were carried by the steam into the liter flask. Once started, the process goes on smoothly and requires no troublesome manipulation. The emanation was allowed to stand in the liter flask 15 minutes before being transferred to the electroscope. The sum of the activities of the evolved and retained emanation is the activity of the total emanation.

In the following table the activities are expressed in arbitrary units, for 1 g. of the mineral. The value given in each case is the mean of two to four concordant determinations.

TABLE 2.

	Activity of retained Emanation	Activity of evolved Emanation	Activity of of total Emanation	Per cent. of of total Emanation Evolved	Per cent. of of Uranium	Activity of per gram Uranium
1	62.8	2.46	65.4	3.76	44.7	146.0
2		6.49	78.6	8.25	54.0	145.6
3	80.0	3.69	83.7	4.41	58.1	144.0

The last column shows a close proportionality between the total amount of emanation and the percentage of uranium in the mineral, as previously shown by Boltwood.

The retained emanation of Sample No. 2 could not be determined in the manner described, owing to the fact that the mineral was not completely disintegrated by treatment with boiling dilute sulphuric and nitric acids.

The sample was easily brought into solution after fusion with potassium acid sulphate. The solution obtained from a known weight of mineral was placed in a small flask, boiled to expel all emanation present, and then sealed up. At the end of a known period of time (about 4 days), the emanation which had formed was boiled off, collected, and its activity determined. The activity of the total emanation was thus calculated by means of the equation, $I_0 = Ie^{\lambda t}$, where λ was taken as 0.173, corresponding to a period of 3.99 days.[1]

It is probable that the emanating power of a compact mineral like pitchblende is negligibly small until the mineral is powdered. If so, the loss of activity must date from the time when the mineral is pulverized. During a few weeks, or even months, after pulverization, loss of emanation will therefore cause an appreciable deficiency in the amounts of the products of rapid decay, A, B and C, only; while the amount of D, period 40 years, will not be noticeably altered. The amounts of E and F which are products of D will also be practically unchanged by loss of emanation. In order that one may know by what fraction the specific activity of a mineral is decreased by the spontaneous loss of emanation after pulverization,

[1] Curie, Compt. rend., 135, 857 (1902).

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it is necessary to know what fraction of the total activity is due to Em + A + B + C The experimental determination was made as follows: A portion of sample No. 1, finely ground was treated with nitric acid, evaporated to dryness and the process repeated three times at intervals of two hours, in order to free the material from Em and allow A, B and C to decay. After the last evaporation, the residue was heated just strongly enough to decompose the nitrates present. The resulting residue, consisting essentially of oxides, was made into films as quickly as possible, and its activity determined in the usual way. Two closely agreeing experiments showed that 52 per cent. of the original activity of the mineral had been removed by the treatment. Therefore the activity due to Em + A + B + C is approximately half the total activity of the mineral.

A similar conclusion is also reached from the following theoretical considerations. Boltwood has shown[1] by direct experiment that the activity of Em + A + B + C is 4.64 times as great as that of the equilibrium amount of radium free from its products. We find, as shown in the following paragraphs, that radium free from its products is 0.53 as active as the equilibrium amount of uranium in a mineral, and, also that the activity of a mineral is 4.54 times that due to the uranium alone. Therefore the activity of Em + A + B + C in a mineral is $\frac{4.64 \times 0.53}{4.54} =$ 0.54 of the total activity. Direct experiment gave 0.52.

The Specific Activity of Uranium in Minerals.

The proper corrections may now be applied to the observed specific activities of the minerals as given in Table 2. The results are given in Table 3.

TABLE 3.

Sample	k_1 Uncorrected	Per Cent. of Em Evolved	Per Cent. of Activity Lost	k_1 Corrected	Amount of Uranium Per gram (P)	$\frac{k_1}{P}$
No. 1	1582	3.76	1.9	1613	0.447	3610
No. 2	1908	8.25	4.1	1990	0.540	3685
No. 3	2018	4.41	2.2	2064	0.581	3552
					Mean	3616

The quantity, 3616, is the specific activity of uranium in minerals. The corresponding constant for pure uranium compounds is 796. The ratio of the two quantities is 4.54. For equal uranium content, minerals free from thorium are 4.54 times as active as pure compounds.

Danne has shown[2] that radium occurs in certain uranium free minerals, from Issy-l'Eveque. A specimen of this material was given to us by Prof. Millikan, who had received the sample from Prof. Langevin. We wish to thank both gentlemen for the specimen. We found that a lump

[1] Am. J. Sci., 21, 413 (1906).
[2] Compt. rend., 140, 241 (1905).

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of the mineral, which contained no uranium, was more active than an equally large lump of pure pitchblende. But when the lump was powdered and spread over a 20-fold greater surface its activity, instead o being increased about 20-fold, as would have been the case with pitchblende, was decreased 70 per cent! *The activity was almost wholly superficial.* When a lump of the mineral was boiled with dilute hydrochloric acid a few minutes, only traces of the substance went into the solution; but 97 per cent. of the activity was removed. The minute residue left upon evaporation of the acid solution, was highly active. Danne has suggested that the radium has been deposited comparatively recently by percolating subterranean waters; our observations tend strongly to confirm this view. The occurence of radium in uranium-free minerals does not invalidate the law of fixed proportions of uranium and radium in minerals; since the law applies only to minerals sufficiently old to have reached equilibrium conditions. It only shows that radium may be separated from uranium by natural, as well as by artificial, processes.

We have shown[1] that, when the activity due to uranium is deducted, the remaining activity of any thorium mineral is proportional to its percentage of thorium.[2] It was also shown that the specific activity of thorium containing the equilibrium amounts of its products is the same in pure compounds as it is in minerals; in this respect thorium differs markedly from uranium. Inasmuch as the activity of a thorium mineral is completely accounted for, thorium cannot be the parent of radium. On the other hand it was important to discover to what extent the activity of uranium and radium and their known products would account for the activity of uranium minerals, free from thorium. A summary of our results on this topic has already been published.[3] The experimental process consisted in the determination, firstly, of the activity due to radium, free from its products, in 1 cc. of a solution which contained no other active element and, secondly of the amount of radium emanation contained in 1 cc. of the solution in terms of the amount associated with 1 g. of pure uranium in a mineral. It was thus found that the activity of the radium (free from its products) contained in a mineral is 0.53 of that of the equilibrium amount of uranium.

The radium solution was prepared from the insoluble residue left after the treatment of a good sample of pitchblende with nitric and hydrofluoric acids. One gram of the residue was boiled with 100 cc. of 15 per cent. sodium carbonate solution for 30 minutes. The residue was filtered out and washed and then dissolved in hydrochloric acid. About 0.3 g.

[1] Am. J. Sci., 26, 433 (1906).

[2] Similar results were also announced by Boltwood and by Dadourian in the same number of the Am. J. Sci. as that which contained our paper.

[3] Abstract of a paper read before the Am. Phys. Soc.; Phys. Rev., Jan., 1907.

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of bismuth chloride was added. The copper, lead, bismuth, etc., were then precipitated with hydrogen sulphide. The sulphide precipitate was several times as active as uranium and probably contained all of the RaF. The filtrate was boiled to expel hydrogen sulphide completely and then oxidized with bromine. The iron was precipitated with ammonia. The filtrate was treated with a little sulphuric acid and the small precipitate of barium (and radium) sulphate was filtered out. The precipitate was then converted into carbonate and the latter into chloride. The solution of the chloride was evaporated to dryness in a platinum dish, taken up in 200 cc. of water and filtered to remove any possible trace of insoluble matter.

Portions of 5 cc. of the radium solution were evaporated on flat platinum plates 6 cm. square. At intervals of about one hour, the residue was dissolved on the plate in a little dilute hydrochloric acid and again evaporated, in order to remove the emanation and the excited activity. During the fourth (the last) evaporation the solution was so manipulated, by means of a bit of bent platinum wire, that the resulting residue of less than 1 mg. weight, was spread evenly over the whole plate. There is no appreciable absorption of the α-ray activity in so thin a film. The activity of the film (with the bit of wire) was determined by comparison with a thick film of uranium oxide of known activity. As the mean of a number of such determinations, the total activity of the radium in 5 cc. of the solution was found equal to the total activity of 0.1237 g. of uranium.

A portion of the radium solution was diluted 20-fold and portions equal to 0.5 cc. of the original solution were diluted with water and placed in 150 cc. flasks. The emanation present was completely expelled by boiling and the flasks were then sealed. After known intervals of 4 to 5 days the emanation was boiled off from each solution, its activity determined and the equilibrium amount calculated in the usual way. The equilibrium amount of emanation of 5 cc. of the original radium solution equaled that for 0.2312 g. of uranium in a mineral. The ratio, $\frac{0.2312}{0.1237} = 1.87$, represents the relative activity of equilibrium amounts of uranium and radium in a mineral. Conversely radium is 0.53 as active as the equilibrium amount of uranium.

Boltwood has shown[1] that radium plus the maximum amounts of Em, A, B, and C is 5.64 times as active as radium alone. His experiments also indicate, as he pointed out, that the activity of the equilibrium amount of any member of a radioactive series is proportional to its range. The range of the α-rays of radium F is 3.85 cm.[2] while that of radium is

[1] Am. J. Sci., 21, 409.

[2] Levin, Am. J. Sci., 22, 8 (1906).

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3.50 ccm.[1] Therefore F is 1.10 times as active as the equilibrium amount of radium alone. Since D is inactive and E gives only β-rays, uranium together with radium and its products are $1.87 + 5.64 + 1.10 = 8.61$ times as active as the radium alone; or $8.61/1.87 = 4.60$ times as active as the equilibrium amount of uranium. Our direct experiments gave 4.54 as the ratio of the activity associated with equal amounts of uranium in minerals and in pure compounds. The close agreement of the two values would seem to indicate that the activity of a uranium mineral (free from thorium) is due solely to uranium and radium and their recognized products.

That radium is a transformation product of uranium is now apparently fully established. The abnormally slow growth of radium in pure uranium[2] is no doubt due to an inactive product of long period compared with radium, between U and Ra. For a time it seemed probable that actinium was this intermediate product; since actinium separated from uranium minerals actually produced radium emanation at approximately the calculated rate[3].

But Rutherford found later[4] that the rate of growth of radium in preparations obtained from the fractionation of actinium solutions, is not proportional to the quantity of actinium present; and concluded that the parent of radium is only accidentally associated with actinium. There is also another weighty reason against the view that actinium is the product in question. The sum of the ranges of actinium and its products is 22.65 cm.[5] while that of radium is 3.50 cm. Therefore actinium and its recognized products should be $22.65/3.50 = 6.5$ times as active as radium, or 3.5 times as active as the equilibrium amount of uranium, considering actinium a member of the uranium series. But the observed activity of uranium minerals is insufficient to account for more than a small fraction of this estimated actinium activity. Boltwood has considered this matter[6] and has suggested that each of the other α-ray changes in the uranium-radium series takes place with the expulsion of four α-particles. Such a view is interesting, but not in harmony with a number of facts, as Boltwood himself admits.

The fact that the activity of uranium ores seems to be fully accounted for by the activity of uranium and radium and their known products,

[1] Bragg and Kleeman, Loc. cit.

[2] Boltwood, Am. J. Sci., 20, 239 (1905); Soddy, Nature, 76, 150 (1907).

[3] Boltwood, Am. J. Sci., 22, 537 (1906); Rutherford, Nature, 75, 270 (1907).

[4] Nature, 76, 126 (1907).

[5] Hahn, Phil. Mag., 12, 253 (1906).

[6] Nature, 75, 223 (1907). In this "Letter to the Editor" which contains no account of experimetal details, Dr. Boltwood states that radium is 0.52 as active as the equilibrium amount of uranium; we found 0.53. He also states that minerals are 5.3 times as active as pure uranium compounds of the same uranium content. This is much greater than the value, 4.54, which we find for the same ratio.

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indicates that but a very small fraction of the activity of a mineral can be due to actinium. If we adhere to the views that but one α-particle is expelled from an atom during a single change, and that activity in any series is even approximately proportional to range; then we must conclude that the number of atoms of actinium changing per second, in a given mass of a mineral, is far less than the number of atoms of uranium changing.

Of course, actinium may not be formed from uranium, but its presence in uranium minerals seems to indicate a genetic relationship. The following hypothesis offers a plausible explanation which is in harmony with the known facts. It is conceivable that atoms of UX may decompose in two ways, each with its own rate of change (such cases are frequent in ordinary chemical decompositions). The more rapid disintegration may yield the radium series; while the other slower disintegration gives the actinium series. If the period of the second sort of change of UX is, say, 0.01 of that of the first; then, for every 101 atoms of uranium changed, one atom of actinium would be formed and disintegrated. Therefore the total activity of actinium and its products would be but a fraction of one per cent. of the total activity of a mineral.

There is perhaps a little evidence that UX does change in two ways. Moore and Schlundt[1] observed that UX apparently has faint α-ray activity which decays with the same period as the β-activity. Levin[2] has confirmed Moore and Schlundt's observations, as has also Mr. G. C. Ashman, working in this laboratory. But Levin has shown that a large part of the so-called α-ray activity is probably due to secondary β-rays. Still, according to Levin, 8 per cent. of the activity of UX may be due to α-rays. Now it is possible that the change involving the expulsion of a β-particle produces, eventually, radium and that giving an α-particle produces actinium. The faint α-ray activity of UX may, according to this view, be due to an abnormally small number of α-particles produced, rather than to a very short range of particles expelled in normal numbers.

As has been stated, uranium is 1.87 times as active as the equilibrium amount of radium; since the range of the latter is 3.50 cm., that of the former should be $1.87 \times 3.50 = 6.65$ cm., if we assume the range proportional to the activity. This estimated range is about twice as great as one would expect, considering Rutherford's experiments on the thickness of air through which the α-rays of uranium, radium or thorium pass before being reduced in intensity to half value[3]. We have made some measurements of the range of uranium essentially according to the method of Bragg and Kleeman[4] using a very uniform film of U_3O_8, made by the

[1] Phil. Mag., 12, 393 (1906).
[2] Physik., 8, 129 (1907).
[3] Rutherford, Radioactivity, 168 (1905).
[4] Loc. cit.

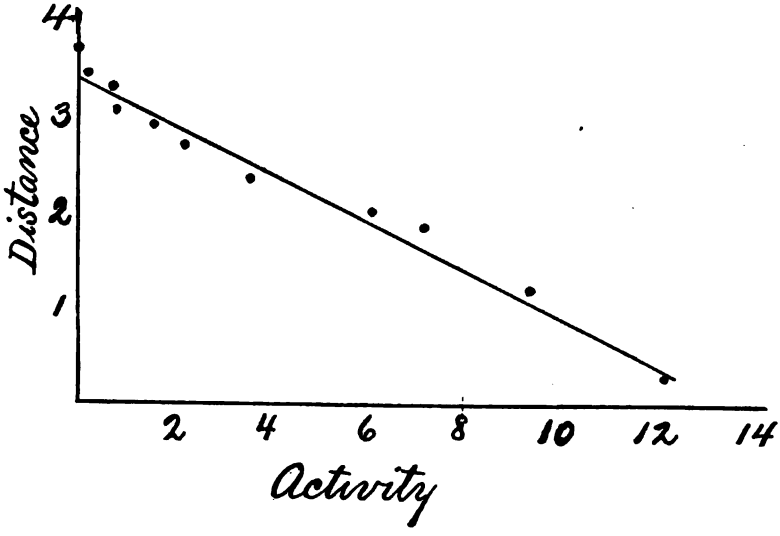
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usual process of sedimentation. The film was 7 cm. in diameter and weighed 43 mg. It was enclosed in a copper cylinder 8 cm. in diameter and 5 cm. high with a wire gauze top and solid base. The film could be placed at any desired distance below the gauze, which was fixed at a distance of 0.5 cm. below the electrode attached to the gold leaf system. The following table gives the observed activities, in arbitrary units for various distances in cm., between the film and the gauze.

TABLE 4.

Distance	0.30	1.20	1.85	2.00	2.35	2.70	2.90	3.05	3.30	3.45	3.70
Activity	12.2	9.4	7.2	6.1	3.8	2.2	1.6	0.8	0.7	0.2	0.0

The results are reproduced graphically in the accompanying figure.



The low specific activity of uranium made it impossible to employ extremely thin films such as Bragg and Kleeman used in determining the range of radium. On account of the appreciable thickness of the uranium film used, the α-ray radiation was not of uniform range, and so did not give results like those obtained with infinitely thin films. Nevertheless the experiment seems to show that the maximum range of uranium is about 3.4 cm. Bragg's experiments[1] on the absorption of the α-rays of uranium by thin sheets of aluminum indicate a range of 3.3 cm. A very plausible explanation of the lack of agreement of the experimental value with that calculated, 6.65 cm., lies in the supposition of a new α-ray product of uranium, with a range of about 3.2 cm. This excess of α-ray activity is not to be accounted for to any appreciable extent, by the α-ray activity of UX, since the latter activity constitutes, at most, but a very

[1] Phil. Mag., 11, 754 (1906).

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small fraction of the total activity of uranium. The new product may be either a very rapidly changing one[1] between U and UX; or it may be inseparable[2] from uranium just as radiothorium is from thorium[3]. Of course there remains the possibility as we at first[4] also suggested that two α-particles are produced directly by the disintegration of each atom of uranium.

It is very probable that altogether there are three α-particles expelled during the several changes accompanying the transformation of an atom of uranium into an atom of radium. If the final product of the uranium —radium series be lead[5]; 8 α-particles of average atomic weight 3.95 are lost by an atom of uranium (atomic weight 238.5) in changing into one of lead (atomic weight 206.9). Of these 8 particles radium, and its products give off 5; leaving 3 for the change of uranium into radium. On this basis, the atomic weight of radium should be 226.65. In a paper just published[6] Mme. Curie shows her earlier value 225, for this constant to be too low, and gives instead 226.45; which is in good accord with the calculated value. The supposed inactive product, of very long period, between uranium and radium may be the third α-ray product of uranium, which may emit α-particles with less than the critical velocity necessary to produce ionization.

Summary.

1. New determinations of the specific activity of uranium minerals were made under conditions so chosen that the α-rays of the active films all reach the limits of their ranges in the air of the ionization chamber. The observed activity has been corrected for the deficiency due to loss of emanation. The specific activity of uranium in minerals is 3616, while the corresponding constant for pure uranium compounds is 796. For equal uranium content, minerals, free from thorium are $3616/796 = 4.54$ times as active as pure compounds.

2. The activity of uranium is 1.87 times that of equilibrium amount of radium (alone).

3. The range of uranium is about 3.4 cm. There is probably a new uranium product which gives α-rays with a range of 3.25 cm.

4, To explain the supposed genetic relationship of actinium to uranium, it is suggested that UX may disintegrate in two ways; the first giving β-

[1] Meyer and Schweidler.—Wien. Ber., Dec. 1904, think uranium may produce an emanation of very short period.

[2] Levin, Physik. Z., 7, 692 (1906), has attempted, in vain, to separate from uranium any radioactive substance other than UX.

[3] See following paper.

[4] Phys. Rev., Jan. 1907.

[5] Boltwood, Am. J. Sci., 20, 253 (1905); 23, 77 (1907).

[6] Chem. News., 96, 127 (1907).

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rays and the inactive product which finally produces radium; the second, much slower change, giving α-rays and actinium, thus:

$$U \rightarrow U' \rightarrow UX \begin{cases} (?) \rightarrow Ra \rightarrow \text{etc.} \\ Ac \rightarrow \text{etc.} \end{cases}$$

Oct. 12, 1907.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO].

THE SPECIFIC RADIOACTIVITY OF THORIUM AND THE VARIATION OF THE ACTIVITY WITH CHEMICAL TREATMENT AND WITH TIME.

BY HERBERT N. MCCOY AND W. H. ROSS.

Received October 14, 1907.

In our first paper[1] on the radioactivity of thorium compounds we showed that, in the case of minerals, when the activity due to uranium was deducted, the remaining activity was strictly proportional to the percentage of thorium present. The following table, taken from the earlier paper, summarizes the results obtained:

TABLE I.

No.	Name	% Th	% U	k_m	k_U	k_{Th}	$\frac{k_{Th}}{P_{Th}}$
1	Orangite.	43.1	7.76	649	255	394	914
2	Thorite	46.6	6.26	664	205	459	985
3	Monazite.	5.27	0.33	60.2	10.9	49.3	935
4	"	15.18	0.46	164	15	149	982
5	"	2.72	0.12	29.8	4.0	25.8	950

Mean = 953

The symbol k_m, represents the specific activity of the mineral, in terms of the activity of 1 sq. cm. of a thick film of U_3O_8 as unity; k_U is the activity due to uranium; $k_{Th} = k_m - k_U$. P_{Th} is the weight of thorium per gram of mineral.

Results similar to these were published by Boltwood[2] in the same number of the Am. J. Sci. as that in which our paper appeared. Boltwood's results were expressed in arbitrary units, but showed just as clearly as do those of Table 1, the constant specific activity of thorium in minerals. A third simultaneous paper, in the same journal by Dadourian[3] contained similar conclusions reached as a result of a different method of investigation; which consisted in the measurement of the intensity of the excited activity obtained from the thorium emanation given off by solutions of minerals. These results were also expressed in arbitrary units.

In the first paper we stated:

"All of the thorium activity measurements, as well as those of uran-

[1] Am. J. Sci., 21, 433 (1906).

[2] Ibid., 21, 409 (1906).

[3] Ibid., 21, 427 (1906).

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ium compounds and minerals, were made with a distance of 3.5 cm. between the active films and the charged electrode. While this thickness of air is sufficient to absorb practically all of the alpha rays of uranium, it is scarcely great enough to absorb completely the more penetrating alpha rays of some of the radium and thorium products[1]. With a greater distance than 3.5 cm. between the films and electrode a somewhat greater activity will be found for uranium and thorium minerals. The general relationship between the radioactivity and the composition of such minerals having now been fully established, we are starting a new series of measurements on minerals with the object of determining their activities under conditions such that the maximum ionizations due to the alpha rays can take place in the space between the film and the electrode." The recent work of Hahn[2] on the ranges of the products of thorium, also emphasizes the necessity of a larger ionization chamber than we first used.

In the new series of measurements, we worked in the manner described in the preceding paper on *The Specific Radioactivity of Uranium*, using the new electroscope, and films of the mineral deposited by sedimentation on flat, rimless plates. Since the earlier work had shown that the specific activity of thorium in its minerals is constant, it was considered unnecessary to repeat the activity measurements of more than three of the minerals in order to determine the exact value of this constant. The new results are given in Table 2. The new value found for the specific activity of uranium in minerals, 3616, was used in calculating the activity due to that element in each thorium mineral.

TABLE 2.

Name	$\% Th$	$\% U$	k_m	k_U	k_{Th}	$\frac{k_{Th}}{P_{Th}}$
Orangite	43.1	7.76	707	281	426	988
Thorite	46.6	6.26	699	226	473	1015
Monazite	15.18	0.46	172	16.6	155.4	1025
					Mean	1009

The mean value of k_{Th}/P_{Th}, 1009, is the specific activity of thorium containing the equilibrium amounts of its products.

We also previously found that the specific activity of thorium in pure ThO_2 obtained in the analyses of minerals by Neish's process[3], was constant and equal to the specific activity of thorium in minerals. But the activity[4] of pure ThO_2 prepared from commercial samples of pure nitrate was always much less than that obtained from minerals by Neish's process[5]. The lat-

[1] Rutherford, Radioactivity, p. 168, 1905; Bragg and Kleeman, Phil. Mag., 10, 318 and 600 (1905).

[2] Phil. Mag., 11, 794; 12, 82 (1906).

[3] This Journal, 26, 780 (1904).

[4] The activities were measured four or five weeks after preparation when the samples had regained the amounts of ThX, etc., corresponding to the amounts of radiothorium present in each case.

[5] Boltwood and Dadourian obtained similar results.

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ter sort contained the maximum or equilibrium amount of radiothorium, while the former evidently did not. It seemed, therefore, as if the technical method of preparation of thorium nitrate was more effective in separating radiothorium from thorium than was Neish's analytical method. We therefore attempted, by various chemical processes, to remove from thorium the whole of the radiothorium, with the object in view of obtaining thorium of minimum activity. As previously announced, we were able by the application of certain processes, many times repeated, to reduce the permanent activity of thorium considerably below that of the least active commercial sample used. But, in spite of the apparently promising results of the preliminary experiments, we did not succeed in separating radiothorium completely from thorium. In fact, it now appears doubtful whether it is possible by chemical treatment to separate any radiothorium from thorium. In a recent paper,[1] Hahn has pointed out that the activity of thorium preparations decreased spontaneously to an appreciable extent in the course of a few years; Boltwood[2] has also observed the same thing. We are able to confirm these observations by new measurements of the activity of preparations made and first measured about one and one-half years ago. Hahn also found thorium preparations nine to 12 years old were more active than those three years old. These facts are explained by Hahn by the supposition that there is an inactive product, which he has called mesothorium, between thorium and radiothorium and that this intermediate product is removed in the process of preparation of pure compounds from minerals; but that the radiothorium remains with the thorium. Hahn first estimated the period of mesothorium to be about seven years; in his second paper[3], he states that his estimate is apparently somewhat too high, but in neither paper does he give the numerical data upon which the estimate is based. According to Blanc[4], the period of radiothorium is 737 days. The low activity of commercial samples of thorium, as observed by Boltwood and by Dadourian, as well as by ourselves, is explained by Hahn as due to the decay of radiothorium with time, rather than to its removal by chemical processes. It is also probable that the decrease in activity of thorium preparations, which we observed after numerous chemical treatments, was the result solely of the decay of radiothorium, (aided by the chemical removal of mesothorium), during the time which had elapsed between the measurements of activity which preceded and those which followed the chemical treatments; in fact our experiments strongly indicate that radiothorium is entirely inseparable from thorium by chemical processes. Of course the indirect

[1] Ber., 40, 1462 (1907).
[2] Am. J. Sci., 24, 93 (1907).
[3] Ber., 40, 3304 (1907).
[4] Physik. Z., 8, 321 (1907).

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separation of radiothorium may doubtless be accomplished by the removal, from time to time, of the mesothorium; the radiothorium will then continue to decay until in the course of 15 or 20 years it has practically completely disappeared.

We found, as shown in our first paper on this subject, that thorium dioxide obtained in the analyses of minerals by Neish's method had the same activity as it had in the original mineral. Neish's process involves one precipitation with oxalic acid; one with potassium hydroxide; and two with nitrobenzoic acid. Boltwood found similar results with thorium dioxide obtained from minerals by analytical processes in which the thorium was separated either by means of repeated treatments with ammonium oxalate or repeated precipitations with sodium thiosulphate. It follows from these results that none of the chemical processes involved removes any appreciable fraction of the radiothorium.

We have made a number of additional experiments in which commercial samples ("A" and "B") of thorium nitrate[1] have been subjected to the various treatments described below and finally converted into thorium dioxide.

(1). Twenty grams of sample A were dissolved in 200 cc. of boiling water and a solution containing one gram of oxalic acid was added; this precipitated about one-eighth of the thorium. The oxalate so obtained was converted into oxide by ignition.

(2). Additional one gram portions of oxalic acid were added to the filtrate from (1), the precipitate being filtered out after each addition; the eighth precipitate was ignited to oxide and constituted sample 2.

(3). Ten grams of sample A were dissolved in 300 cc. of boiling water and precipitated with 12 g. of sodium thiosulphate in 100 cc. of water. The boiling was continued one or two minutes. The precipitate was filtered out and dissolved in dilute nitric acid, the excess of the latter was nearly neutralized with ammonia and the whole process repeated. After eight precipitations in this manner the material was converted into oxide.

(4). Five grams of sample A were dissolved in 200 cc. of water and precipitated, at boiling temperature, with five grams of potassium chromate in 50 cc. of water. The precipitate was filtered out and dissolved in dilute nitric acid; the solution was diluted and the thorium chromate again precipitated from the hot solution by the addition of ammonia. The solution was acid, in reaction, at the end of the precipitation. After eight precipitations in this way, the solution in nitric acid was treated with an excess of oxalic acid; the oxalate was washed and converted into oxide.

[1] The samples were made by the firm of C. A. F. Kahlbaum; the oxide obtained by ignition was analyzed by Neish's method and found to be practically chemically pure in each case.

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(5). Two grams of the sample A and 10 g. of barium chloride were dissolved in 200 cc. of water and a solution of 6.5 g. of ammonium oxalate was added; this was just sufficient to precipitate both the thorium and the barium as oxalates. Another portion of 6.5 g. of ammonium oxalate was now added to dissolve the thorium as double oxalate. After being heated to boiling, the residue of barium oxalate was filtered out and the filtrate was treated with 10 g. more of barium chloride. This process was repeated until 7 precipitations had been made. The barium oxalate was removed from the last precipitate by means of dilute hydrochloric acid: the thorium oxalate remaining was converted into oxide by Neish's method.

(6). Ten grams of sample A were dissolved in 400 cc. of water and precipitated with an excess of freshly distilled ammonia. The separated precipitate was dissolved in nitric acid and the process repeated 100 times; the last precipitate was converted into oxide. Analysis showed that this oxide contained 4.6 per cent. of impurity, due to the action of the alkaline solutions on the glass vessels used.

(7). Twenty grams of solid nitrate, sample B, were ground in a mortar with an excess of concentrated ammonia; the hydroxide so formed was filtered out, and ignited to oxide. The oxide so obtained is much more compact than that formed by the direct ignition of the nitrate.

(8). Fifteen grams of sample B were dissolved in 300 cc. of water and precipitated with hydrogen peroxide, at a temperature of about 70°. The separated precipitate was dissolved in nitric acid; the thorium was again precipitated from the dilute solution by the addition of 45 g. of ammonium acetate and 35 cc. of hydrogen peroxide. The whole process was repeated until 40 precipitations had been made; the last precipitate was purified by Neish's method and converted into oxide.

The activities of these preparations were measured in the old way (films in tins with rims and 4.5 cm. between films and electrode), but the results as given in Table 3 have been multiplied by the factor 1.12, which is the ratio of the activity as determined in the new way (flat films and 8.5 cm. ionization space) to that determined in the old.

TABLE 3—ACTIVITIES OF SAMPLES OF THORIUM DIOXIDE.

	Chemical treatment	Date of precipitation. Oxides from sample A	Activity on May 8th, 1906	Activity on September 12th, 1907
1.	1 pptn. oxalic acid.....	Apr. 6, 1906	529	417
2.	8 pptn. oxalic acid.....	Apr. 6, 1906	529	423
3.	8 pptn. thiosulphate.....	Apr. 4, 1906	529	414
4.	8 pptn. chromate.....	Apr. 9, 1906	547	421
5.	7 pptn. barium oxalate....	June 11, 1906	...	420
6.	100 pptn. ammonia.....	Apr. 3, 1906	510[1]	402[1]
		Oxides from sample B	Feb. 24, 1906	Sept. 12, 1907
7.	1 pptn. ammonia.....	Nov. 11, 1905	477	410
8.	40 pptn. hydrogen peroxide	June 28, 1906	...	385

[1] The values given have been corrected for the 4.6% impurity contained in the sample.

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As has been shown, one precipitation with oxalic acid, (which is included in Neish's analytical method), does not remove any radiothorium from thorium. Since the activities of samples (2) to (5) were practically the same as that of sample (1) at each time of measurement, as shown in Table 3, it follows that none of the processes used in making these samples effects any separation of radiothorium. The activity of sample (6) is a little low, but the difference, about 4 per cent., may be only experimental error; at most since there were 100 precipitations, one precipitation with ammonia removes but 0.04 per cent. of the radiothorium present. It would seem from a comparison of the activities of (7) and (8) that 40 precipitations with hydrogen peroxide remove a small portion of the radiothorium; yet the lower activity of (8) may be due to a different cause: the incomplete removal of mesothorium from (7) at the time of its preparation from the nitrate Nov. 11, 1905. This point will be considered further in subsequent paragraphs. The isolation of radiothorium from thorianite[1] and from pure thorium nitrate[2] seems to indicate the possibility of separating radiothorium by chemical processes; but these results may have been accomplished through the separation of mesothorium, which in time changed spontaneously into radiothorium.

The specific activities given in Table 3 refer to thoria containing the amounts of ThX and subsequent products, corresponding to the amounts of radiothorium in the samples, since the activity measurements were made about one month after the last chemical treatment. As most of the chemical processes, used in the attempts to remove radiothorium, readily remove ThX, the activity of any sample immediately after its preparation was much less than one month later. Rutherford and Soddy[3], who were the first to observe this fact in the case of thorium precipitated with ammonia, found that the final activity was about 4 times as great as the initial. We found the ratio of final to initial activity to be approximately 2.5 for the various samples of thoria prepared from sample A of nitrate.

The corresponding ratio for thoria separated from minerals in analyses by Neish's method was about 3.2. The greater ratio in the case of thoria rich in radiothorium was observed by us at the time of the measurements made in May, 1906, Table 3, and was considered, at that time, to prove conclusively that thorium itself is active. And, although the available data were not exact, we estimated that the specific activity of thorium dioxide alone was probably between 100 and 130. Hahn, in his recent paper already referred to, has observed the greater ratio of maximum to minimum activity for samples rich in radiothorium and has pointed out that this shows finally and conclusively that thorium itself is active, that

[1] Ramsay, J. chim. phys., 3, 617 (1905); Hahn, Ber., 38, 3371 (1905).
[2] Blanc, Physik. Z., 7, 620 (1906).
[3] Phil. Mag., Sept., 1902.

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is, that thorium alone emits α-rays. We do not wish to make any claim of priority on this point, as this is the first publication of our observations; but we do wish to emphasize the fact that Hahn's conclusion is correct.

As was just stated, the data from which we first estimated the activity of thorium alone were not exact; this was due to the fact that the numerous precipitations with ammonia required for the removal of ThX and its products[1] introduced silica and other impurities from the glass. An improved method for the separation of ThX and all subsequent products from thorium has been worked out by Mr. G. C. Ashman and one of us.[2] It was found that precipitation of thorium with meta-nitrobenzoic acid leaves ThX and ThA in the solution; four precipitations at intervals of two hours give finally chemically pure thorium dioxide, which is entirely free from ThX and its subsequent products. From the observations of the minimum and maximum activities of the two samples of thoria, one containing but little radiothorium, the other freshly prepared from a mineral, the specific activity of thorium dioxide, free from radiothorium and all other active products, was found to be 105. The activities of the equilibrium amounts of radiothorium and of ThX and subsequent products for one gram of thorium dioxide were 182 and 655 respectively. These values refer to flat films and an ionization space of 8.5 cm. between the film and the electrode, the measurements having been made in the electroscope described in the preceding paper.

If the chemical processes involved in the preparation, from a mineral, of any sample of a pure thorium compound remove all or part of the mesothorium, the activity of the sample will fall to a minimum, in the course of time, and then increase again, as Hahn has stated. It follows also that this minimum activity will be *perfectly definite*, provided the whole of the mesothorium is removed and that the purification processes are all carried out at one time, say within a period of one month. The ratio of this minimum activity to the activity of thorium containing the equilibrium amounts of all its products is a fraction, which is a function of (1) the period of mesothorium; (2) the period of radiothorium; (3) the activity of thorium alone; (4) the activity of thorium and its subsequent products. Conversely, if the value of this minimum be known, the period of mesothorium may be calculated, since all of the other data are now available.

Rutherford[3] has developed the general equation for the variation with time of the number of particles of one radioactive body, produced by the disintegration of another. This equation applies to the formation of

[1] Rutherford and Soddy, Loc. cit.

[2] The results will be published soon.—H. N. McCoy.

[3] Radioactivity, 331, (1905).

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radiothorium from mesothorium. Let λ_1 and λ_2 represent the disintegration constants and n_0' and n_0'' the equilibrium numbers of particles per gram of thorium dioxide, of mesothorium and radiothorium respectively. The number of particles, n'', of radiothorium formed in time, t, from n'_0 particles of mesothorium, which contained no radiothorium at time zero, is given by equation (1)

$$n'' = \frac{n_0'\lambda_1}{\lambda_2 - \lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) \qquad (1)$$

But $$n_0'\lambda_1 = n_0''\lambda_2$$

Therefore $$n'' = \frac{n_0''\lambda_2}{\lambda_2 - \lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) \qquad (2)$$

If, from a quantity of thoria which contained the equilibrium amounts of all its products, the mesothorium only were removed completely at time zero, then $(n_0'' - n'')/n_0''$ would represent the fraction of the equilibrium number of particles of radiothorium left in the thoria at the time, t. The fraction, $(n_0''-n'')n_0''$, decreases with time and reaches a minimum, which may be called m, at a time which depends only on the periods of the two substances concerned. If we take the activity of one gram of thorium dioxide alone as 105 and the activity of the equilibrium amounts of its products as 837 the minimum specific activity of the thoria, corresponding to a minimum content of radiothorium, is equal to $837m + 105$.

We have found that the present activity of a sample of thoria, made by strongly igniting sample A of thorium nitrate, is 476. If we take this activity as the minimum, we may write $837m + 105 = 476$; from which $m = 0.443 = (n_0'' - n'')n_0''$. From this last relationship and equation (2), the value of λ_1 may be found; and from λ_1 the period of mesothorium. The value thus found for the last mentioned constant was 5.4 years; it may actually be greater, however, since the minimum activity may be less than 476. If the period is 5.4 years, the minimum activity will be reached in 4½ years from the date of preparation. Since the specific activity of this sample was 579 on Dec. 8, 1905, it was then probably about 2.0 years old. If so, it is now, Sept., 1907, about 3.8 years old; and although the minimum activity will not be reached for 9 or 10 months (assuming the period of mesothorium to be 5.4 years) the total activity will diminish less than one per cent. in this time. From these considerations it seems probable that the period of mesothorium is not far from 5.5 years. If so, the minimum activity will be reached in 4.6 years. This conclusion is in good agreement with the changes of activity of samples which have been under observation for about 1½ years.

On April 4th to 9th, 1906, samples (1) to (4), Table 3, were subjected to chemical treatment which probably removed all of the mesothorium

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present at that time. The mean activity of these samples was 534 on May 8, 1906, and 418 on Sept. 12, 1907. In the interval, 492 days, the radiothorium present on May 8th, 1906, would decay to $e^{-492\lambda_2} = 0.630$; the products of radiothorium would disappear in the same proportion. Now the specific activity of thorium dioxide itself is 105. If no radiothorium had been formed from the new mesothorium produced from thorium during the interval of about 525 days between the date of preparation and that of final measurement, Sept. 12, 1907, the activity of the samples would have been $0.630(534 - 105) + 105 = 375$ on the latter date. But some radiothorium must have been produced from the mesothorium formed from thorium during this interval and it is easy to show that the activity of the radiothorium so formed would be, for $t = 525$,

$$837\left\{1 - \left[\frac{\lambda_2}{\lambda_2 - \lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) - e^{-\lambda_2 t}\right]\right\} = 30.$$

The calculated specific activity on Sept. 12, 1907, of samples 1 to 4 is, therefore, $375 + 30 = 405$. The observed activity was 418.

Table 4 gives a summary of the results, of a similar sort, obtained with other samples already described as well as with two additional samples, 9 and 10.

Sample 9 was thorium dioxide prepared by Neish's method from a sample of "partially purified oxalates," made by the Welsbach Light Company.[1]

Sample 10 was thorium dioxide obtained in the analyses of orangite and thorite[2].

TABLE 4.

Samples	Date of Preparation	Date and Activity		Date and Activity		Calculated Activity
1-2-3-4	Apr. 4-9, 1906	May 8, 1906;	534	Sept. 12, 1907;	418	405
6	" 3, "	" " "	510	" " "	402	390
7	Nov. 11, 1905	Feb. 24, "	477	" " "	410	370
9	May 8, 1906	July 6, "	854	" 23 "	610	625
10	Dec. 2-6, 1905	Feb. 9, "	947	" 28 "	621	630

With the exception of the results for sample (7), the values calculated and observed are in fairly good agreement. The higher observed activity of (7) is very probably due to incomplete removal of mesothorium at the time of the preparation of the oxide from the nitrate, Nov. 11, 1905; since the chemical treatment consisted only in grinding the solid nitrate with concentrated ammonia, filtering and igniting. The difference in activity of (7) and (8), Sept., 1907, (Table 3) may also be due to the incomplete separation of mesothorium from (7), rather than to the removal from (8) of part of the radiothorium by the chemical treatment employed.

[1] We wish to express our thanks to Mr. H. S. Miner, chemist for the Welsbach Company, who has supplied us with this as well as a number of other samples of thorium products.

[2] See Table XIV, Am. J. Sci., 21, 443 (1906).

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On the other hand, it is very probable that the chemical processes carried out in the preparation of all the other samples, removed practically all of the mesothorium contained in them. Thus the activity of a sample of thorium dioxide, made by ignition alone of sample A of nitrate, had an activity of 476 in Sept., 1907, while samples 1 to 4, made from the same sample of nitrate, had a mean activity of 418.

Summary.

1. The specific activity of thorium in minerals was found to be 1009 (the unit being the activity of one sq. cm. of a thick film of U_3O_8) when measured under such conditions that all of the α-rays reach their maximum ranges in air.

2. The direct separation of radiothorium, from thorium by chemical processes is remarkably difficult, if not impossible. This question is being studied further in this laboratory.

3. The diminutions of activity of thorium, which we previously observed after certain chemical treatments, are completely explained by Hahn's hypothesis of an intermediate product, mesothorium, between thorium and radiothorium; which product is easily removed by the chemical treatments; in consequence of which the radiothorium decays with time and thus causes the observed changes of activity.

4. If all of the mesothorium be removed, at one time, in the process of preparation from a mineral of pure thorium dioxide, the activity of the latter will fall to a definite minimum. From the activity of a sample of thoria, supposed to have reached this minimum, the period of mesothorium was calculated to be 5.5 years.

5. The quantitative changes of activity with time, of a number of samples of thoria agreed well with the values calculated on the assumption of a period of 5.5 years for mesothorium.

Oct. 12, 1907.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE BUREAU OF STANDARDS, NO. 3].

THE ATOMIC WEIGHT OF HYDROGEN.

BY WILLIAM A. NOYES.

Received September 10, 1907.

Some years ago the writer[1] carried out a series of determinations of the quantitative composition of water, from which the value 15.896 was calculated for the atomic weight of oxygen on the hydrogen basis. The opinion was expressed, in the paper, that the true value was probably within one part in a thousand of this number, and that it was rather below than above the value reported. Several years later Morley[2] pub-

[1] Am. Ch. J., 12, 441 (1890).

[2] Smithsonian Contributions to Knowledge, 1895: Am. Ch. J., 17, 267 and 396; Z. physik. Chem., 17, 87.

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lished an account of his elaborate determinations of the densities of hydrogen and oxygen, and of the composition of water by weight, which led him to the value 15.879 for oxygen, or 1.00762 for hydrogen (O = 16). Meanwhile Richards[1] had shown that copper oxide retains occluded gases obstinately, a fact which was partly known to me at the time of my work, but which was not as carefully considered as it should have been. There was obtained in each of my experiments, at the end, a small amount of gas which was assumed to be nitrogen on the basis of one or two rather imperfect analyses of the earlier samples. The weight of this gas, calculated as nitrogen, was subtracted from the weight of the hydrogen, giving, on the average, a correction of about one part in a thousand. Several years after the publication of Morley's results it occurred to me that this gas came, very probably, from the copper oxide and that its weight should be subtracted from the weight of the oxygen instead of from that of the hydrogen. On applying the correction in this manner the value 15.879 (or 1.00765) was found.

While this agreement with Morley's value was gratifying and the fact was stated to a few personal friends, it did not seem proper to publish a statement about the matter until the surmise could be confirmed by new experimental evidence.

In addition to the desire of confirming or refuting the above explanation of my earlier results, several reasons have made it seem worth while to undertake a new determination of this constant. Hitherto our accurate knowledge of the composition of water has rested on Morley's work alone. He secured so high a degree of concordance in his results, and he exercised such an extraordinary degree of care at every point that the results obtained by all other observers must be considered as having only confirmatory value in comparison[2]. It seemed worth while, if possible, to secure a similar order of accuracy by a different method.

Richards and Wells[3] have recently given us a very accurate determination of the ratio between silver and chlorine, but the exact value for the atomic weight of chlorine is still in doubt because the ratio between silver and oxygen is not satisfactorily known[4]. A determination of the ratio between hydrogen and chlorine has been carried out at this Bureau, and by using hydrogen generated in the same manner for that determination and for the determination of the composition of water, a very direct comparison between oxygen and chlorine has been secured. As the atomic weights of more than forty elements have been determined in their relation to silver or the halogens, or both, the fundamental importance of the ratios of chlorine and silver to oxygen is apparent.

[1] Pr. Am. Acad., 26, 276 (1891).
[2] This will be discussed further in a later paper.
[3] This Journal, 27, 459.
[4] Guye and Ter Gazarian : Compt. rend., 143, 411.

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Finally, it seemed possible to so carry out the work as to secure some evidence with regard to the question of change of weight in a chemical reaction in which a large amount of energy is dissipated. This phase of the problem was suggested to me while considering the claim made by Prof. S. M. Babcock some years ago that ice loses weight when it melts. He proposed the theory that the loss of weight was intimately connected with the gain of energy by the ice as it melts. If this were true, hydrogen and oxygen should gain weight when they combine to form water. It may be said, at once, that the results to be given are not conclusive on this point. So far as they have any bearing on the question they indicate a loss rather than a gain in weight when hydrogen is converted into water.

Apparatus.—The apparatus used in the work was, in part, very similar to that used in the previous investigation.[1] Five series of determinations have been carried out. In the first four of these the hydrogen and oxygen were obtained by the electrolysis of dilute (15 per cent.) sulphuric acid. In the last series the gases were generated by the electrolysis of a six to eight per cent. solution of barium hydroxide.

The purifying train will be easily understood from the figure. In the first three series of experiments and in all but the last three determinations of the fourth series, the hydrogen was passed at first through a tube of common glass filled partly with platinized asbestos and partly with copper gauze, and the oxygen was passed through a similar tube filled partly with platinized asbestos, partly with asbestos mixed with lead chromate. These tubes were heated to 300°–350°. In the last three experiments of the fourth series hard glass tubes were substituted for the common glass, so that a higher temperature could be used, and in the fifth series hard glass tubes filled with platinized quartz were used. The platinized quartz was prepared by moistening the quartz, which had been heated and quenched in water, with a solution of chlorplatinic acid and reducing the latter in a current of hydrogen. Each gas then passed through a serpentine tube about four meters in length and of 8 mm. internal diameter. These tubes contained a fifteen per cent. solution of potassium hydroxide, in which was dissolved a small amount of lead oxide. Sulphur compounds present in the hydrogen were reduced to hydrogen sulphide as the mixture passed over the platinized asbestos and copper, and the sulphur of the hydrogen sulphide was retained by the lead as lead sulphide. Only a very small amount of lead sulphide was deposited during the passage of more than 1,000 liters of hydrogen through the asbestos. When the barium hydroxide was used as an electrolyte, the serpentine tubes were replaced by bulbs to collect the condensed water and the solution formed by the deliquescence of the potassium hydroxide.

[1] Am. Ch. J., 12, 441.

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The union between the hard and soft glass was made by grinding the joint and then melting in it a very small amount of Khotinsky cement. Ample evidence is given below that these joints were perfect.

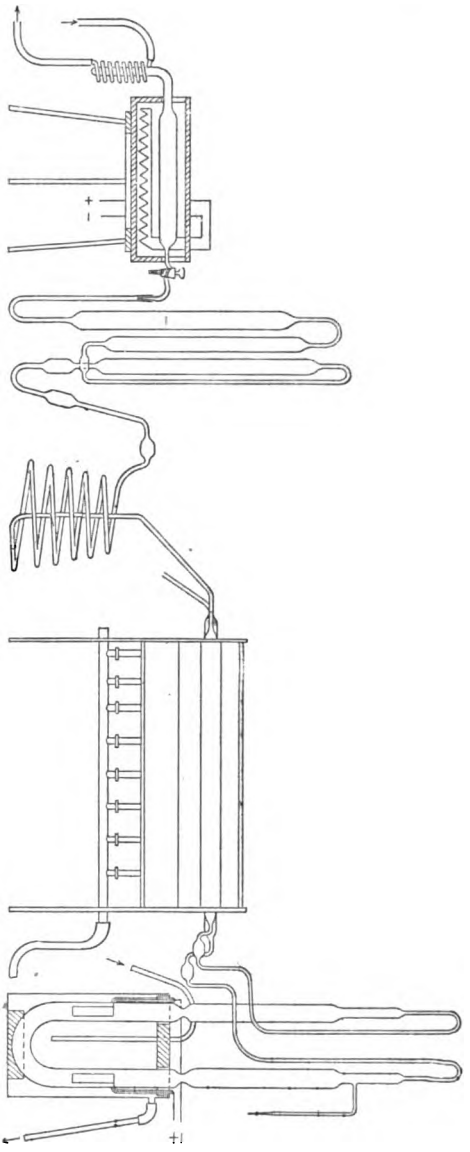


FIG. 1

The gases passed next through the tubes containing potassium hydroxide in the form of sticks and then through two or three tubes 15 mm. in diameter and 25 cm. long, filled with phosphorus pentoxide which had

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been sublimed in a current of oxygen. When not in use these tubes were always sealed and great care was exercised to avoid the entrance of moist air from the exits where the gases were delivered for use. If the phosphorus pentoxide were to become moist on that side, there would be danger that the gases might carry some of the moisture away with them.

The electrolytic apparatus containing the sulphuric acid or solution of barium hydroxide consisted of a U-tube with platinum electrodes. The limbs of the tube were about 35 mm. in diameter and 55 cm. long. It was filled about two-thirds full at first and when the solution became too concentrated, water, recently boiled and cooled out of contact with the air, was introduced through the small tube shown on the oxygen side of the apparatus. It was easy to do this without allowing any air to enter, but after each filling a considerable amount of the gases were generated before further use of them for a determination. The water used for preparing the original solution and for subsequent dilutions was purified by redistilling distilled water with the addition of an alkaline solution of potassium permanganate and collecting the portion that was free from ammonia.

The resistance of the sulphuric acid in the apparatus was 4–5 ohms, while that of the solution of barium hydroxide was considerably greater. It was necessary to cool the electrolytic apparatus with a pretty rapid current of water through the jar containing it. The electrical current used had a pressure of 120 volts, and was reduced by means of a rheostat placed in series with the electrolytic cell. With the sulphuric acid electrolyte a current up to 15 amperes could be used, giving six liters of hydrogen an hour. With the barium hydroxide it was not considered safe to go beyond four liters an hour, because of the greater resistance and consequent heating of the solution.

Copper Oxide.—In the first three series of experiments copper oxide was used to convert the hydrogen into water. In the first three experiments copper oxide prepared by precipitating copper sulphate with a hot solution of sodium hydroxide was used. The precipitate was washed by decantation until it became colloidal, and then thoroughly on a Buchner funnel. This oxide retained a trace of sulphate, which was reduced by the hydrogen to sulphur dioxide and the latter was found in small amount in the water obtained. Only two determinations were made with this oxide. Seven determinations were made with a sample of copper oxide purchased as pure from Kahlbaum. It contained arsenic and other impurities. As these determinations formed a part of the first series, the results of which are rejected for reasons to be given below, they need not be discussed further here. The copper oxide for the remainder of the first and for the second and third series was prepared by precipitation of a hot solution of copper sulphate, Rochelle salt and

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sodium hydroxide with glucose. The cuprous oxide obtained could be washed indefinitely and all sulphates were very completely removed. After ignition in a current of oxygen the oxide retained a very small amount of carbon dioxide, but as this appeared as a gas at the end of the experiment and the amount could be determined, no serious error can have arisen from this source. The same copper oxide was used repeatedly and after several determinations the carbon dioxide nearly disappeared.

Balance and Weights.—The balance used was made by Ruprecht, of Vienna, and was designed to carry a maximum load of one kilogram on each pan. The air of the balance case was dried by means of a rapid current of air blown through two wash bottles containing concentrated sulphuric acid and a little chromic anhydride. The spray of sulphuric acid carried by the current was removed by passing through two tubes, the first containing glass wool and the second cotton wool. The current of air was stopped ten to twenty minutes before the weight was determined. During the last series of experiments the balance case was enclosed in a larger glass case and the air within the latter was dried by means of large dishes of calcium chloride set on top of the inner case. For determinations in which the weight of the hydrogen was involved, the weight was always determined twice at an interval of one-half hour or more and with the current of air passing into the case during a part of the interval. In 100 pairs of weights taken from the notebook at random, the average difference was 0.05 mg., and the maximum difference 0.12 mg.

Weights.—The weights used were carefully calibrated by Mr Pienkowsky, of this Bureau, at the beginning of the work, a second time after they had been in use for ten months, and a third time at the completion of the investigation, a little more than two years after it was begun. The largest change observed in any of the weights used was 0.04 mg.; while none of the platinum weights changed more than 0.01 mg. The aluminum rider gained 0.014 mg. A recalculation of the amounts of hydrogen in the last series showed that the use of the new corrections caused no change exceeding 0.14 mg. in the weight of the hydrogen for any experiment of that series, while the algebraic sum of the changes for the five experiments of the series was 0.09 mg. or one part in two hundred and fifty thousand of the weight of hydrogen used.

The calibration of the weights was, of course, to a vacuum standard. Since the substances to be weighed were always enclosed in a glass apparatus whose volume remained constant and which was counterpoised by another glass apparatus of very nearly the same volume and weight, no vacuum correction in the ordinary sense was required. For our present purpose it is most convenient to assume the brass weights in air as standard. If we do this, the platinum weights will appear too heavy be-

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cause they displace less air in proportion to their weight. This requires a correction of 0.087 mg. which must be added for each gram of platinum weights used. For convenience, a table was prepared which included this correction for the platinum weights with the other corrections as determined in the comparisons of the weights.

Purity of the Gases Used.

As with all atomic weight determinations, the value of the present investigation depends in very large measure upon the purity of the substances weighed—in this case, hydrogen, oxygen and water. The impurities which might be present were: in the hydrogen:—nitrogen, oxygen, water, phosphorus pentoxide and compounds of sulphur; in the oxygen there might be the same impurities with hydrogen in place of oxygen; in the water:—sulphur dioxide or carbon dioxide.

Nitrogen.—In the former series of determinations there was obtained at the end of each experiment a small amount of gas which, when calculated as nitrogen corresponded to about one one-thousandth of the weight of hydrogen used. It was found quite early in the present investigation that when the water is removed from the apparatus containing reduced copper it carries with it a small quantity of hydrogen, probably hydrogen which has been occluded by the copper. The gases were analyzed in a narrow eudiometer of such length that when the amount of gas was small, the column of mercury in the eudiometer was 600-650 mm. in length so that the gas was under a pressure of only about one-seventh of an atmosphere. In this way quantities of nitrogen as small as 0.02 mg. could be measured.

As will be seen below, it was possible to secure copper oxide so pure that only very small amounts of nitrogen were found at the close of experiments in which it was used. But the best evidence of the freedom of the hydrogen from nitrogen was obtained in the last series. From 22.6 grams of hydrogen and the equivalent amount of oxygen there was obtained only 0.59 mg. of nitrogen. This includes all of the nitrogen in the oxygen as well, and all of the leakage of the stop-cock during seven weeks. If we assume that two-thirds of this nitrogen came from the hydrogen it is only one part in 57,000 by weight, or one part in 800,000 by volume. On the basis of this evidence it is assumed that all of the hydrogen used was free from nitrogen and no correction has been made for the small quantities found in each experiment. It is not believed that the error from this source can be so great as one part in 20,000.

Incidentally these experiments have demonstrated the possibility of using, without leakage, ordinary, well ground and carefully lubricated stopcocks under such conditions that they are subjected to atmospheric pressure with a vacuum inside of the apparatus for days together. The

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well known rubber lubricant was used. It was made by heating a mixture of 16 parts of vaseline, 8 parts of pure rubber and 1 part of paraffin to a temperature of 350°-400° for several hours until it was thoroughly homogeneous. For warm weather, or for a stopcock liable to become warm, a little more parraffin was added.

Oxygen.—After the investigation had progressed so far that it was evident that the results differed from Morley's by a much larger amount than can be accounted for by accidental errors, it was feared that the hydrogen contained a trace of oxygen which escaped conversion into water as the gas passed over the platinized asbestos and copper gauze, especially as the latter were heated to only about 350°. To test this possibility the purified and dried hydrogen was passed through a hard glass tube containing platinized asbestos heated to dull redness and then through a phosphorus pentoxide tube. The latter was closed with stopcocks and was weighed each time filled with hydrogen and with the use of a counterpoise. The earlier experiments gave appreciable amounts of water (1 mg. from 1 g. of hydrogen) which was in part, at least, from the asbestos, and even after the asbestos had been heated almost daily for six weeks some water was still obtained (1.1 mg. from 2.74 g. of hydrogen)[1].

But when some of the same hydrogen was passed over strips of palladium heated to 360° in an electrical airbath, 3.78 g. of hydrogen gave a change of weight of —0.08 mg. It still seemed possible that a trace of oxygen mixed with *dry* hydrogen might pass the palladium without change. To test this a small T-tube was introduced between the hydrogen generator and the palladium tube in such a manner that the lower arm could be filled with dry oxygen. This would then find its way into the hydrogen by slow diffusion. The amount of oxygen retained in the arm of the T-tube was found in two experiments to be 1.68 and 1.94 mg. respectively, while in three experiments in which similar amounts of oxygen were allowed to diffuse into the hydrogen before it entered the palladium tube there were found 2.29, 2.21 and 2.58 mg. of water. While the conditions were such that an exact quantitative agreement could not be expected, the experiments demonstrated that minute quantities of oxygen can be readily detected by this method.

After the close of the last series of experiments the hydrogen was tested by passing it through the tube containing strips of palladium heated to 360° and then through the pentoxide tube. In these experiments there were passed 2.74, 2.92 and 2.92 g. of hydrogen respectively, while the changes in weight of the phosphorus pentoxide tubes were —0.44, +0.14

[1] It seems possible that this water may have passed through the walls of the red-hot tube during the five hours of the experiment. It seems not improbable that glass, as a viscous liquid, may dissolve a small amount of water and that such dissolved water might slowly diffuse through to the inner surface. This question is worthy of further study.

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and +0.04 mg., quantities scarcely beyond the errors of weighing and insignificant in proportion to the weight of the hydrogen.

Water.—The experiments just described demonstrate the absence of water in the hydrogen used in the last series. After the close of the third series, hydrogen from the apparatus was passed through the phosphorus pentoxide tube at the rate of six liters an hour for five successive days, 12.6 g. of hydrogen in all. The changes in weight of the pentoxide tube were —0.01, +0.63, —1.06, —0.33, —0.14 mg.; in all a net loss of 0.76 mg., or one part in 17,000. At the close of the fourth series 3.78 g. of hydrogen were passed through the pentoxide tube at the rate of six liters an hour with a change in weight of — 0.04 mg. and a similar amount passed though the tubes containing heated palladium, gave a change of weight of —0.08 mg.

It seems, therefore, that the phosphorus pentoxide used to dry the hydrogen retained its efficiency to the end. The first of these tubes showed considerable deliquescence, caused by the water still remaining in the hydrogen after it passed the sticks of caustic potash, but the last tube showed no sign that it was affected by the moisture.

Phosphorus Pentoxide.—Morley[1] has shown that one liter of a gas at ordinary temperatures carries with it only 0.00002 mg. of vapor of phosphorus pentoxide. This would correspond to 0.0002 mg. in one gram of hydrogen, an amount without any significance in comparison with the degree of accuracy now possible in determinations of atomic weights. It is believed that the crystalline phosphorus pentoxide obtained by sublimation, adhering as it did closely to the walls or the tube and fibers of glass wool, on which it was deposited, was much less likely to be carried on mechanically by the current of gas than the finely pulverulent pentoxide in its usual form would have been.

Compounds of Sulphur.—After the close of the third series a careful test for compounds of sulphur was made by bringing together the hydrogen and oxygen, delivered by the apparatus, in such a manner that they could be burned and the water collected. The hydrogen was evolved at the rate of six liters an hour, the most rapid rate used in the atomic determinations. The water obtained weighed 112.4 g. A little bromine water and 0.1 g. of sodium carbonate were added to it and it was evaporated to dryness in a platinum dish on an electric plate. The residue was acidified with hydrochloric acid, filtered from silica which came from the glass apparatus in which the gases were burned and the filtrate was tested with a solution of barium chloride. A trifling turbidity appeared slowly, estimated to be less than that occasioned by 0.1 mg. of sulphuric acid in a solution of similar volume and character. This would corre-

[1] J. Am. Chem. Soc., 26, 1171.

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spond to one part of sulphur dioxide, by weight, in 250,000 parts of the hydrogen.

Purity of the Oxygen.—The experiment just described demonstrates the practical absence of sulphur in the oxygen. Tests for moisture also showed that no amount which could be of significance, was present.

Purity of the Water.—In the two experiments referred to above in which copper oxide prepared by the precipitation of copper sulphate with sodium hydroxide was used, some sulphur dioxide was found. When pure copper oxide was used no evidence of its presence was ever obtained. In all experiments in which the sulphuric acid electrolyte was used the water was tested with a dilute solution of potassium permanganate (1 cc. = 0.05 mg. available O) and with N/10 barium or sodium hydroxide, with phenolphthalein as an indicator. The amounts required never exceeded 0.1 cc. of the permanganate and 0.03 cc. of the N/10 alkali, to produce a coloration in from 20 to 40 cc. of the water. The water of the last two series, especially, was frequently tested for hydrogen peroxide but none was found.

First Series.

This series consisted of twenty experiments. In the earlier experiments the weight of the hydrogen was determined by the gain in weight of a piece of apparatus containing copper oxide, the water formed by the oxidation of hydrogen being condensed within the same apparatus. The method used will be clear from Fig. 1. About 160 g. of copper oxide were placed in the part of the apparatus represented as lying in the electrical airbath. After sealing the apparatus at the end designed to collect the water, its volume was determined by hydrostatic weighing and a tube of almost the same volume and weight was prepared. The apparatus was then placed in the airbath and heated to 400° while it was connected with a Sprengel air-pump and exhausted. A phosphorus pentoxide tube, sealed to the pump, was interposed between the pump and the apparatus and also a small McLeod guage[1]. The exhaustion was carried to the hundred thousandth of an atmosphere or further and the heating continued for some time.

For connection with the pump and for other similar connections used throughout the work, the end of the apparatus was drawn out to fit a glass socket connected with the pump. The joint was completed by melting a little Khotinsky cement between the parts in contact. Such a joint, if properly made, will hold for an indefinite length of time against atmospheric pressure, without any leakage that can be measured. The

[1] The bulb of the gauge had a capacity of about 16.5 cc. To avoid contaminating the mercury by contact with india rubber, the gauge was sealed below to an upright glass tube about 12 mm. in diameter. In this was a light, loosely fitting glass plunger. By pressing the plunger down the mercury could be easily forced up into the gauge for the measurement.

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parts are easily separated by gentle warming and cleaned by warming and wiping with cotton followed by a cloth moistened with alcohol.

After cooling, the apparatus was rinsed with distilled water, wiped with a clean cloth and placed on the balance. The tare and weights were placed on the other pan, the current of dry air started through the balance case and the weighing completed, with the use of the rider, on the following day.

The apparatus was then connected with the source of hydrogen, the copper oxide heated to 300°-350° and hydrogen passed in for four to six hours. A coil of small tin pipe conveying cold water was placed around the part of the apparatus outside of the airbath to condense the water. By means of the rheostat connected with the electrolytic apparatus it was easy to regulate the supply of hydrogen to correspond with the rate at which it was oxidized by the copper oxide. The operation was always stopped before the copper oxide was all reduced and by heating for a short time after closing the stopcock, the conversion of the last of the hydrogen to water was completed.

After cooling and standing over night, as before, the weight of the

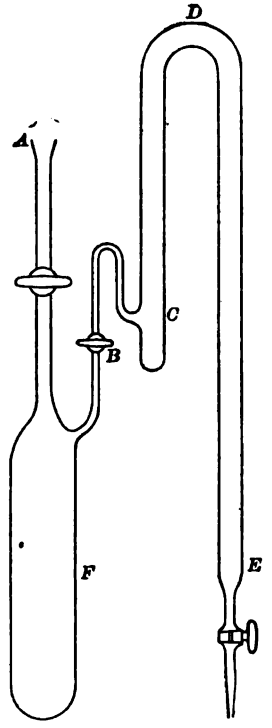


FIG. 2.

hydrogen, which had been introduced, was determined. The apparatus was then connected at A with the apparatus shown in Fig. 2, the other

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end, E, of the apparatus being connected with the Sprengel pump. This apparatus was filled with phosphorus pentoxide from C to E. The end at C is designed to collect the phosphoric acid resulting from the deliquescence of the pentoxide, while it is quite necessary that the part C D should be directed up and not down, as otherwise the syrupy phosphoric acid runs down into the unchanged phosphorus pentoxide and seals the tube. The apparatus was, of course, previously exhausted and weighed, using a glass counterpoise of nearly the same volume and weight.

After exhausting the connecting tubes by means of the pump, the bulb F was placed in a freezing mixture of ice and sulphuric acid, the stopcock B was closed and the stopcock of the copper oxide apparatus opened. By passing hot water through the coil of tin pipe surrounding the part of the apparatus containing the water, the latter was easily distilled into F in the course of two to four hours. By opening B occasionally any permanent gas brought over with the water vapor was allowed to pass on to the pump and transferred by means of the latter to the eudiometer in which the gas was analyzed. When permanent gases were allowed to accumulate in F the passage of the water vapor was checked and condensation occurred in the connecting tubes. This difficulty occurred especially in the last two series, when considerable hydrogen was present, but was rarely experienced in the first three series. After the water had been transferred to F and the bulb containing the copper had been heated to 400° for a short time, the apparatus containing the water was removed and replaced by a tube containing phosphorus pentoxide and the heating of the apparatus continued for some time longer. Only a few milligrams of water were obtained in this manner. The apparatus containing the reduced copper was then cooled and weighed next morning, the loss of weight as compared with the original weight giving the weight of the main portion of the oxygen.

The reduced copper still retains, however, at 400°, either water or hydrogen which cannot be removed by the process described. To obtain this the apparatus was again placed in the electrical airbath, heated to 400° and the copper oxidized as far as possible by means of oxygen from the electrolytic apparatus. The water formed was then removed by connection with a phosphorus pentoxide tube and heating as before. After cooling and weighing, the apparatus was now ready for a second experiment.

In seven determinations of this series the hydrogen was absorbed in palladium and its weight was determined twice, first by the loss in weight of the palladium tube and second by the gain in weight of the copper oxide tube. The palladium tube was given the form shown at A in Fig. 3. The palladium foil was furnished by Heraeus. It was 0.05 mm. in thickness. Three hundred and sixty grams of it were cut into strips

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4 cm. wide and these were wound in three rolls which were placed in the tube A. Before use the rolls were placed in a hard glass tube and heated to redness in a current of oxygen. After placing it in A it was heated

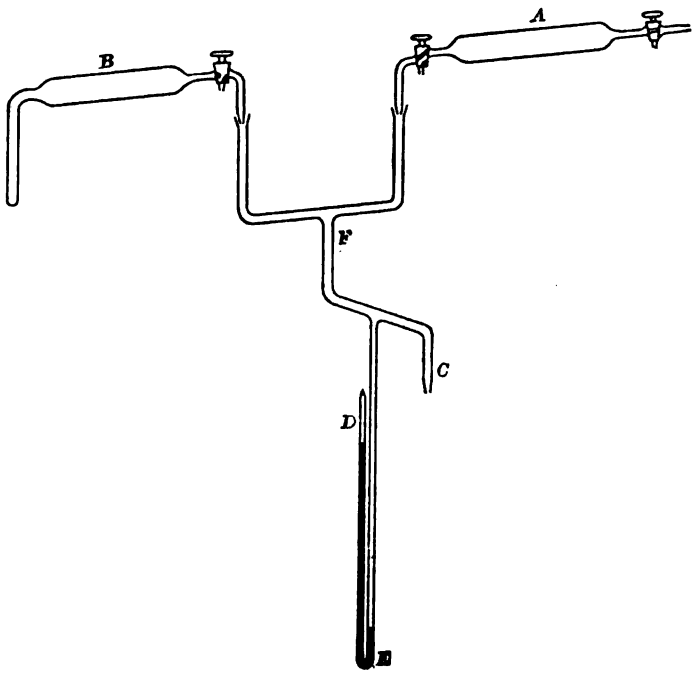


FIG. 3.

for some time in a current of hydrogen till thoroughly dry. It was then cooled and charged with hydrogen and when saturated a current of hydrogen was passed through the tube for a short time. The tube was weighed with a counterpoise and after standing over night, in the same manner as described for the copper oxide tube.

The arrangement employed for the transfer of the hydrogen to the copper oxide tube is shown in Fig. 3. For greater simplicity the airbaths in which A and B were placed and supported are not shown. The tube C was connected with the Sprengel pump. After exhaustion of the connecting tubes the connection with the pump was cut off by means of a stopcock situated close to the connection with C. The palladium tube was then slowly heated while the copper oxide tube was heated to 350°. The pressure in the system could be easily followed by means of the shortened manometer D E. This contained a small amount of air at D but not enough to carry the mercury beyond the bend at E when the pressure in F fell to zero. The heating of A was so regulated that the pressure was usually a little below that of the atmosphere, the reaction in B

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proceeding most rapidly under slightly reduced pressure. The 360 g. of palladium absorbed 2.3 g. of hydrogen and of this 2 g. could be easily expelled at 150°-160°. This amount could be transferred from A to B in three to five hours. The rate of transfer could be followed by the amount of water condensed in B. When enough water had collected, the stopcock of the copper oxide tube was closed and the palladium was allowed to cool till most of the hydrogen in the connecting tubes had been reabsorbed. The stopcock of the palladium tube was then closed and the hydrogen in the connecting tubes pumped out into a eudiometer and measured. This hydrogen varied from 0.02 to 0.14 mg. according to the time allowed for the palladium to cool.

The twenty experiments of the first series gave for the atomic weight of hydrogen as calculated from the weight of the hydrogen and the weight of the oxygen, 1.00819 ± 0.00010, and from the weight of the hydrogen and water 1.00821 ± 0.00010. This is a smaller probable error than has been obtained by any previous observer except Keiser and Morley, but it was found at the close of the series that it is subject to a constant error which is, apparently, about three times the "probable error."

It was known at the beginning of the investigation that copper oxide at 400° would retain a small amount of water. It was hoped, however, that this might be made very small and also that by making the end of one experiment the beginning of the next the total amount of water retained would be so nearly constant that it would not affect, appreciably, the result of any experiment in the series after the first. At the close of the last experiment of this series it was thought wise to test this point by transferring the copper oxide to a hard glass tube and heating it in a current of oxygen. To my surprise there was obtained 37.7 mg. of water, although the previous oxidation and heating at 400° had given only 3.3 mg. If we assume this water to have come from the last six experiments of the series, which formed a continuous set in which the end of one experiment was the beginning of the next, the value for the six determinations becomes 1.00782 as calculated from the hydrogen and oxygen or 1.00791 as calculated from the hydrogen and water. It was at once decided to reject the determinations thus far made and which had taken about a year's time and to begin a new series in which this source of error should be eliminated, if possible.

Second Series. Hydrogen from Sulphuric Acid, Weighed Twice.

In this series the hydrogen was weighed in palladium and also after transfer to the copper oxide tube as described above. In order to increase the quantity of hydrogen and reduce the error, after the water had been removed and the copper reoxidized, a second quantity, and in one case a third quantity, of hydrogen was introduced and the water removed. Finally the reduced copper was transferred to a hard glass tube

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and oxidized in a current of oxygen and the amount of water formed was determined. The oxygen used was partly from the S. S. White Dental Manufacturing Company and was purified by passing it over red-hot copper oxide and through wash bottles containing a solution of sodium hydroxide and over phosphorous pentoxide. In some of the experiments electrolytic oxygen was used.

Several experiments were made to determine the amount of water taken up by the copper oxide in the transfer to the hard glass tube. In a similar manipulation with dry copper oxide there were obtained 2.63, 1.30, 5.32 and 2.45 mg. of water. This would correspond to an average error of about one part in 10,000. It has not been thought best to apply any correction for this error, partly because of the uncertainty in its amount but chiefly because it is probably balanced by small errors in the opposite direction, due to the retention of water by the copper oxide even after several hours at a red heat in a current of oxygen, and to the retention of a trace of water by the walls or lubricant of the copper oxide apparatus. There is good reason, however, for believing that the error from each of these sources is very small.

Seven determinations were made in this series but in one of them the weight of the oxygen was lost. The results were as follows:

WEIGHTS OF HYDROGEN. SECOND SERIES.

	Grams H CuO tube	Grams H Pd tube	Mg. H in T tube	Mg. H from Cu	Cor. H CuO	Cor. H Pd	Average H
1.	3.72469	3.72689	0.15	0.07	3.72462	3.72667	3.72565
2.	3.80383	3.80280	0.17	0.05	3.80378	3.80258	3.80318
3.	3.75898	3.75886	0.18	0.10	3.75888	3.75858	3.75873
4.	2.96309	2.96357	0.05	0.03	2.96306	2.96349	2.96328
5.	2.11437	2.11366	0.08	0.03	2.11434	2.11355	2.11395
6.	3.53126	3.53173	0.19	0.04	3.53122	3.53150	3.53136
7.	3.53963	3.53982	0.19	0.04	3.53959	3.53959	3.53959

WEIGHTS OF OXYGEN AND WATER. SECOND SERIES.

	Grams O from loss of CuO	Mg. N	Mg. CO_2	Mg. water by reoxidation	Grams O corrected	Grams water
1.	29.56469	0.76	0.28	15.26	29.57891	33.30408
2.	30.16645	0.37	2.33	20.25	30.18400	33.98748
3.	29.81141	0.32	0.79	23.28	29.83358	33.59127
4.	23.49099	0.13	0.60	29.61	23.51987	26.48379
5.		0.20	1.16	27.65		18.89214
6.	27.99401	0.38	0.89	36.36	28.02910	31.56024
7.	28.05652	0.24	0.22	40.13	28.09619	31.63554

ATOMIC WEIGHT OF HYDROGEN. SECOND SERIES.

	From H:O	From H:H_2O
1.	1.00765	1.00767
2.	1.00800	1.00799
3.	1.00792	1.00795
4.	1.00792	1.00790
5.		1.00795
6.	1.00791	1.00792
7.	1.00785	1.00786
Mean	1.00787	1.00789
	± 0.00003	± 0.00003

Mean of all, 1.00788 ± 0.00002

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Third Series. Hydrogen from Sulphuric Acid Weighed after Conversion to Water by Copper Oxide.

In this series hydrogen directly from the electrolytic apparatus was passed into the copper oxide bulb and converted into water. The purpose of the series was more especially to determine whether the purity of the hydrogen had been increased by absorption in the palladium. The results of the series are not as concordant as those of the second but they indicate that the hydrogen directly from the electrolytic apparatus is, if anything, a little lighter and, presumably, a little more pure than after it has been absorbed in palladium. The results were as follows:

WEIGHTS OF HYDROGEN AND OXYGEN, THIRD SERIES.

	Grams H by gain of CuO	H from Cu	Grams H corrected	Grams O by loss of CuO	Mg. N	Mg. CO_2	Mg. water by reoxidation
1.	2.44282	0.03	2.44279	19.34104	0.16	0.10	56.79
2.	2.18741	0.02	2.18739	17.33722	0.10	0.05	25.98
3.	2.75132	0.03	2.75129	21.80908	0.18	0.05	34.60
4.	4.00068	0.06	4.00062				62.31
5.	4.04061	0.04	4.04057	32.04471	0.17	0.06	32.41

ATOMIC WEIGHT OF HYDROGEN. THIRD SERIES.

	Grams O corrected	Grams water	Atomic Weight from H:O	Atomic Weight from $H:H_2O$
1.	19.39757	21.84042	1.00746	1.00746
2.	17.36305	19.55117	1.00784	1.00780
3.	21.84345	24.59389	1.00764	1.00768
4.		35.75073		1.00803
5.	32.07689	36.11762	1.00772	1.00772
			Mean 1.00767	1.00774
			± 0.00006	± 0.00006

Mean of all 1.00771 ± 0.00004

It will be noticed that the amounts of carbon dioxide found are much smaller, owing to the fact that the copper oxide had been freed from it by repeated use. The amount of nitrogen was also smaller, perhaps because of the simpler manipulations involved.

Fourth Series. Hydrogen and Oxygen From Sulphuric Acid Combined by Means of Palladium.

With the best manipulation which it has been possible thus far to secure, the use of copper oxide involves several sources of small constant errors. It is hoped that these errors do not, in the aggregate, exceed one part in 10,000, but it seemed very desirable to find some radically different method which should avoid the use of copper oxide. Such a method consists in absorbing hydrogen in palladium and converting it into water by means of oxygen. This method has already been used by Keiser[1] but his method of manipulation compelled him to use comparatively small amounts of hydrogen and the degree of concordance which he was able to secure was not such that his value for the atomic weight of hydrogen can be used to decide between Morley's value and that found here.

[1] Am. Ch. J., 20, 733.

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The problem seemed at first a very simple one but several months were spent in fruitless experiments before a satisfactory method of manipulation was found.

The 360 grams of palladium foil previously used were placed in a somewhat wider tube and were kept from direct contact with the glass by means of small glass beads strung on platinum wires. The stop-cock at one end of the tube was replaced by a tube having a capacity of about 50 cc. At the beginning the palladium tube was heated and charged with hydrogen and partially exhausted several times to remove moisture. It was then heated to 380°-400° and exhausted until the hydrogen showed a residual pressure of 0.50 to 0.70 mm. as measured by the McLeod gauge. At this pressure and temperature 360 g. of palladium retain only 2-3 mg. of hydrogen and the amounts of hydrogen given out for small changes of pressure are as follows:

0.40 to 0.50 mm.	0.11 mg. H
0.50 " 0.60 "	0.10 " "
0.60 " 0.70 "	0.094 " "
0.70 " 0.80 "	0.087 " "
0.80 " 0.90 "	0.080 " "
0.90 " 1.00 "	0.073 " "
3.90 " 4.00 "	0.044 " "
16.90 " 17.00 "	0.020 " "

A change of temperature of 10° for pressures less than 1 mm. corresponds to a change of 0.03 mg. in the amount of hydrogen retained. At the end of an experiment it was easy to bring the apparatus to a condition of temperature and pressure closely approximating that at the beginning and by means of the table a correction of sufficient accuracy could be applied.

After exhausting, and measuring the temperature and pressure as described, the apparatus was allowed to cool, rinsed with distilled water, wiped, placed on the balance and on the following morning it was weighed. It was then charged with hydrogen (about 2.3 grams) and weighed again on the morning of the third day. The apparatus was then connected with the oxygen side of the electrolytic generator. The palladium tube was inclined so that the water formed ran down into the receptacle at the end. The oxygen entered rapidly for a few minutes but the heat generated soon caused the pressure of the hydrogen to increase and check the current. The oxygen then continued to enter slowly, with the stopcock partly closed, for two or three hours. After that the rate at which the oxygen was taken changed quite suddenly, so suddenly that the first time the experiment was tried the electrolyte was drawn over and the electrolytic apparatus was broken. From this time to the end the entrance of the oxygen was regulated by the stop-

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cock and was allowed to enter as rapidly as it was thought desirable to run the generator. More than enough oxygen to combine with the hydrogen present was easily introduced. On the fourth day, after weighing, the apparatus was charged again with hydrogen.

On the fifth day the manipulation varied. In some cases oxygen was admitted in excess as on the third day. In other cases, as the end of the oxidation of the hydrogen approached, the apparatus was weighed roughly at intervals and the admission of the oxygen was stopped while 5-10 mg. of hydrogen remained unoxidized. By this method of manipulation a day was saved. On the sixth day, or, when an excess of oxygen was admitted, on the fifth, a small excess of hydrogen was admitted. It was necessary to wait till the following day before weighing.

On the sixth or seventh day, according to the method of manipulation chosen, the water and excess of hydrogen were removed and the apparatus brought back to a condition for the beginning of a new experiment. A receptacle similar to that described on page 1728 was used for the water. On account of the hydrogen which accumulated rapidly in the bulb with the water and stopped the current of water vapor, it was found desirable to give the bulb a capacity of about 100 cc. Any nitrogen present was, of course, carried over with the first portions of the water vapor and hydrogen and this part of the gas was collected and analyzed separately. At the close of the removal of the water, the receptacle for the water was replaced by a phosphorus pentoxide tube which permitted of a free connection between the palladium tube and the pump for the measurement of the residual pressure. It was necessary to heat the palladium tube at least two hours in the electrical airbath to secure constant conditions for the measurement of the residual pressure. This was not understood in the earlier determinations of this series and may be one reason why some of the results are not very satisfactory.

In the results which follow, the amounts of nitrogen and carbon dioxide are given as an indication of the magnitude of the errors which may have been occasioned by traces of these gases or by leakages, but no correction for these gases has been applied.

Theoretically, the weight of the apparatus at the end of an experiment should be the same as at the beginning. Practically, it was almost always heavier because of the retention of a small amount of water. When the hydrogen was allowed to accumulate in the receptacle for water the moisture would condense in the connecting tubes and stopcocks and if allowed to remain for a short time in contact with the lubricant of the stopcock, could not be entirely removed. In some cases minute drops of water could be seen within the bore of the stopcock and these would not evaporate during any reasonable length of time. The gain in weight

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of the apparatus during the experiment was, accordingly, assumed to be due to water which had been retained and was added to the weight of water found directly. In cases where condensation was avoided this amount of water was very small or even became negative. (See the following series).

WEIGHTS OF HYDROGEN AND OXYGEN. FOURTH SERIES.

	Grams H	Mg. cor. for changes of l and P	Mg. H recovered	Grams H corrected	Mg N	Mg CO_2	Grams O
1.	2.31840	−0.05	39.19	2.27916	0.48	0.02	18.08455
2.	4.13630	−0.06	8.90	4.12734	0.50	...	32.76527
3.	4.18248	+0.24	7.16	4.17556	0.52	0.02	33.13449
4.	4.19599	−0.51	2.02	4.19346	0.15	0.16	33.27384
5.	2.31593	−0.01	8.46	2.30746	...	...	18.30863
6.	4.60148	−0.23	4.33	4.59692	0.11	0.08	36.48543
7.	4.63931	+0.14	3.20	4.63625	0.07	0.07	36.79354
8.	4.57292	+0.18	0.36	4.57274	0.02	0.28	36.28696

WEIGHTS OF WATER AND ATOMIC WEIGHT OF HYDROGEN.

	Grams of Water	Mg. Water retained	Grams Water corrected	Atomic Weight From H:O	Atomic Weight From $H:H_2O$
1.	20.29807	63.21	20.36128	1.00823	1.00830
2.	36.87182	18.61	36.89043	1.00774	1.00780
3.	37.30667	1.20	37.30787	1.00818	1.00821
4.	37.46202	2.51	37.46453	1.00822	1.00831
5.	20.61671	− 3.14	20.61357	1.00825	1.00839
6.	41.07653	5.09	41.08162	1.00795	1.00797
7.	41.41452	14.53	41.42905	1.00806	1.00808
8.	40.85460	3.74	40.85834	1.00813	1.00817
			Mean,	1.00809	1.00815
				±0.00004	±0.00005
			Mean of all,	1.00812	±0.00003

Fifth Series. Hydrogen and Oxygen From Barium Hydroxide, Combined by Means of Palladium.

The manipulation in this series was essentially the same as in the fourth series. The series has much greater value than the former one, partly as shown by the concordance of the results, partly because the processes of manipulation had been more thoroughly mastered and partly because the electrolyte used gives a greater probability of purity for the hydrogen. In those experiments in which oxygen was introduced last, a small quantity was left in the bore of the three-way stopcock and was usually found in the subsequent analysis of the first portions of gas removed. In one experiment of this series only one-half the quantity of hydrogen was used and too much oxygen was admitted by mistake. This so complicated the manipulation that the experiment was unsatisfactory and it has been omitted from the table. It gave the values 1.00814 and 1.00823.

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WEIGHTS OF HYDROGEN AND OXYGEN. FIFTH SERIES.

	Grams H	Mg. cor. for changes of t° and P	Mg. H recovered	Grams H corrected	Mg. N	Mg. CO_2	Mg O	Grams O
1.	4.61443	—0.07	2.56	4.61180	0.11	0.17	...	36.60909
2.	4.62877	00.0	5.19	4.62358	0.08	0.03	0.13	36.69575
3.	4.60386	—0.02	5.31	4.59853	0.22	0.00	1.31	36.50484
4.	4.56300	+0.04	4.72	4.55832	0.06	0.00	0.29	36.17887
5.	4.21188	—0.04	7.85	4.20399	0.11	0.00	0.11	33.37000

WEIGHTS OF WATER AND ATOMIC WEIGHT OF HYDROGEN.

	Grams Water	Water retained	Grams water corrected	Atomic Weight From H:O	Atomic Weight From H:H_2O
1.	41.21934	1.71	41.22105	1.00779	1.00779
2.	41.30740	9.07	41.31647	1.00798	1.00806
3.	41.09872	3.40	41.10212	1.00776	1.00780
4.	40.74186	—2.82	40.73904	1.00795	1.00790
5.	37.56732	6.04	37.57336	1.00782	1.00786
			Mean,	1.00786	1.00788
				±0.00003	±0.00003
			Mean of all,	1.00787	±0.00002

The mean of the four series, giving them equal weight, is 1.00787 from the hydrogen and oxygen and 1.00791 from the hydrogen and water. The second and fifth series have, however, much greater weight than the third and fourth, and when we consider, further, that there was probably a trifling loss of water, especially in the third series, the value **1.00787** seems to be the most probable result which can be calculated from the work.[1]

It has seemed of interest to recalculate Morley's results on the oxygen basis for comparison with the result here given.

ATOMIC WEIGHT OF HYDROGEN, MORLEY'S RESULTS.

1.	1.00765	1.00778
2.	1.00751	1.00766
3.	1.00768	1.00774
4.	1.00755	
5.	1.00773	1.00750
6.	1.00773	1.00778
7.	1.00777	1.00786
8.	1.00764	1.00761
9.	1.00759	1.00752
10.	1.00752	1.00737
11.	1.00746	1.00734
12.	1.00744	1.00771
Mean,	1.00761	1.00763
	±0.00002	±0.00003
Mean of all,	1.00762	±0.00002

[1] The mean of the results of the 23 determinations in which the hydrogen and oxygen were weighed is 1.00791 and the mean of the 25 determinations in which the hydrogen and water were weighed is 1.00794. The mean of all, considered as a single series of 48 determinations, is 1.00793 ± 0.00002.

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The difference between this result and that given above is greater than can be accounted for on the basis of accidental errors. While the average of the results of the best determinations by either observers approaches more nearly to the result of this investigation than to Morley's value, it does not seem justifiable to calculate a mean on such a basis. For reasons which will be given in a later paper the most probable value which we can get at the present time seems to be the average between Morley's value and that here given. That average is **1.00775.** Morley's value and my own each differ from this by one part in 8,000.

Change in Weight of the Hydrogen When Converted Into Water.

As was stated in the introduction, one purpose of this investigation was to secure, if possible, some evidence of a change of weight which might occur in a reaction in which a large amount of energy is dissipated. In twenty-five experiments the same hydrogen was weighed, first, as absorbed in palladium and, second, after conversion into water by means of the copper oxide. The results were as follows:

Gain of CuO	Loss of Pd	Diff. Mg.	Gain of CuO	Loss of Pd	Diff. Mg.
1.04216	1.04295	+0.79	0.95151	0.95207	+0.56
1.46493	1.46642	+1.49	1.98130	1.98053	—0.77
0.96114	0.96231	+1.17	1.82248	1.82205	—0.43
1.51279	1.51296	+0.17	2.04840	2.04816	—0.24
1.17961	1.17973	+0.12	1.71048	1.71042	—0.06
1.22273	1.22268	—0.05	1.96621	1.96648	+0.22
1.13563	1.13541	—0.22	0.99685	0.99707	+0.22
1.30184	1.30150	—0.34	2.11434	2.11335	—0.79
1.22851	1.22699	—1.52	2.20439	2.20472	+0.33
0.99563	0.99600	+0.37	1.32683	1.32678	—0.05
1.24243	1.24270	+0.27	2.07207	2.07281	+0.74
1.24639	1.24754	+1.15	1.46752	1.46678	—0.74
1.52682	1.52706	+0.24	36.72299	36.72562	+2.63

An examination of these results shows that in fourteen experiments the hydrogen as weighed in the palladium appeared heavier, while in eleven experiments the hydrogen after conversion into water appeared heavier. The average difference between the two weights of a given quantity of hydrogen was 0.52 mg. or one part in 3,000 while the average amount by which the hydrogen as weighed in the palladium appeared heavier was 0.11 mg. or one part in 14,000. It is clear that these results do not justify any conclusion either way with regard to a change in weight of the hydrogen during the reaction other than that if any change of weight occurs it must be very small. It seems scarcely possible that a change of so much as one part in 10,000 of the weight of the hydrogen takes place. It is, possibly, of interest to note that so far as the results furnish any indication whatever, they point toward a trifling loss of

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weight, a result which would agree with Landolt's elaborate study of the question.[1] It is hoped that this problem may be taken up again by a method capable of giving more accurate results.

BUREAU OF STANDARDS,
Washington, August, 1907.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY NO. 147].

THE STEREOCHEMISTRY OF INDIGO. PRELIMINARY COMMUNICATION.

BY K. GEORGE FALK AND J. M. NELSON.

Received September 28, 1907.

Organic compounds which contain a double bond are capable in general, of existing in two geometrical-isomeric forms. The following lists include a number of these compounds of which one or both of the isomers are colored.

Double bond between two carbon atoms (>C=C<). (When the spacial relations were not given with this group of compounds, the lower melting form was assigned the *cis* structure).

	Cis Form		*Trans* Form	
Substance	M.P.	Color	M.P.	Color
Dibenzoyl ethylene[2]	111°	intense yellow	134°	colorless
Diethoxynaphthostilbene[3]	185–186°	yellow	...	"
Benzaldesoxybenzoin[4]	88–89°	yellow	101–102°	"
Diphenyldinitroethylene[5]	105–106°	yellow	186°	deeper yellow
Piperonylacrylic acid methyl ester[6]	107°	yellow	111°	almost white
α-Benzal-γ-diphenylitaconic acid[7]	...	yellow	...	colorless
" " anhydride[7]	218°	red	267°	"
Dibenzalsuccinic acid[7]	218°	yellow	254°	"
" anhydride[7]	263°	yellow	...	"
Oxidation product of β-benzoylpropionic acid[7]	sublimes	red	sublimes	yellow

The general conclusion to be drawn from the accompanying tables is that *if a compound exists in two geometrical isomeric forms and one of these isomers is colored, the other isomer will either be colorless or possess a different color from the first.* For the special classes of compounds considered, the following relations may be deduced:—

For compounds containing a double bond between two carbon atoms the *cis* forms are more deeply colored.

For oximes, the *anti* forms have higher melting points, are more deeply colored and less soluble.

For hydrazones the *anti* (α) forms have lower melting points, are more deeply colored, and more soluble.

For diazosulphonates, the *syn* forms are more deeply colored.

[1] Z. physik. Chem., 55, 589.

[2] Ber., 33, 3795; 35, 168. [3] J. pr. Chem., 47, 72. [4] Ber., 34, 3897.

[5] Ibid., 34, 619. [6] Ibid., 24, 618. [7] Werner "Stereochemie", p. 214.

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OXIMES	Syn R.C.H ‖ N.OR′			Anti′ R.C.H ‖ R¹O.N		
	M.P.	Color	Solubility	M.P	Color	Solubility
Quinone dioxime[1]	——	Light grey	——	——	Yellow	——
" " diacetate[1]	147°	——	more	190°	——	less
m-Nitrobenzaldoxime sodium[2]	——	Light yellow	——	——	yellow	——
4-Chlortoluquinone oxime[3]	165°	" "	easily	170°	brownish yellow	difficultly
Acetyl " " " [3]	141-142°	" "	"	158-159°	amber yellow	"
4-Bromtoluquinone oxime[3]	178-180°	" "	"	186°	brownish yellow	"
Acetyl " " " [3]	131-132°	" "	"	166-167°	amber yellow	"

HYDRAZONES	Syn—β— R.C.Ac ‖ R′HN.N			Anti—α— R.C.Ac ‖ N.NHR′		
	M.P.	Color	Solubility	M.P.	Color	Solubility
Benzaldehydephenylhydrazone[4]	136°	white		152°	almost colorless	
Nitroformaldehydephenylhydrazone[5]	84.5–85.5°	golden yellow	difficultly	74.5–75.5°	orange red	easily
Nitrovalerianicaldehydephenylhydrazone[5]	92.5–93°	" "	"	51.5–52°	" "	"
Benzoylformaldehydephenylhydrazone[5]	138°	yellow	"	114°	orange	"
" -*o*-nitro- " [5]	141.5–142.5°	golden yellow		113°	orange red	
" -*m*- " " [5]	149–150°	orange brown	difficultly	139–140°	orange yellow	easily
Phenylhydrazonecyanacetic ester [6]	82°		more	125°		less
m-Nitro " " [7]	124–125°	light brown	difficultly	136–137°	yellow	easily
p- " " " [7]	184°	yellow	"	168°	"	easily
o- " " " [7]	146°		"	116°	light yellow	"
α-Naphthylhydrazonecyanacetic ester[8]	147°	yellowish brown		105°	brownish red	

[1] Ber., **28**, 340; **20**, 613; **21**, 428. [2] Ibid., **28**, 2013. [3] Ann., **303**, 16.

[4] Ber., **31**, 1249. [5] Ibid., **34**, 2001. [6] J. pr. Chem., **49**, 321. [7] Ibid., **51**, 219. [8] Ibid., **52**, 160. A number of other derivatives of the hydrazone cyanacetic esters are described, but the colors of the α and β isomers are not given.

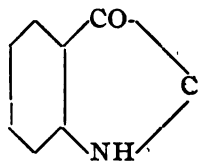
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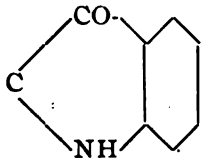
For diazocyanides, the *anti* forms are more deeply colored and have higher melting points.

The conclusions for the different classes of compounds are uncertain to

DIAZO COMPOUNDS.	Syn M.P.	Syn Color	Anti M.P.	Anti Color
Benzenediazo-K-Sulphonate[1]		intense orange		light yellow
o-Chlor " " " [2]		intense red		yellow
p-Chlor " " " [3]		light red		"
p-Brom " " " [3]		"		"
m-Brom " " " [3]		reddish orange		"
2,4-Dibrom " " [3]				"
2,4-Diiod " " [3]		light orange		"
Potassium diazobenzene-*o*-sulphonate[4]		yellow		light yellow
p-Toluenediazo-K-sulphonate[5]		reddish yellow		colorless
α-Naphthalenediazocyanide[6]	57-58°		116°	reddish brown
β- " " [6]	51-52°	yellow	131°	red
Anisol " [7]	50-51°	orange red	121-122°	brownish red
p-Nitrodiazobenzenecyanide[8]	28-29°	yellowish brown	86°	fiery red
p-Chlor " " [8]	29°	yellow	105-106°	yellow or brown
p-Brom " " [6]	42°	yellow	129-130°	brown
p-Iod " " [6]	48°	yellowish brown	152°	reddish brown
o-Brom " " [6]	51°	yellow	107-108°	
2,4-Dibrom " " [6]	70-71°	yellow	141°	reddish brown
3,4- " " " [6]	56-57°	yellow	100-101°	brown
2,5- " " " [6]	42-43°		122-123°	brick red
3,5- " " " [6]	60°	yellowish red	85°	
2,6- " " " [6]	44-45°	yellow		
2,4,6-Tribrom " [6]	59-60°	yellow	147°	brownish red
2,4,5- " " [6]	55°	yellow	100-101°	red

a greater or less extent, but the general conclusion is the point to which it is desired to draw attention. Since this is only a preliminary paper, the application of this principle to other compounds, such as the salts of nitrophenols, certain derivatives of succinylosuccinic ester and of dibenzalacetone, will not be made here[9].

The structural formula of indigo is doubtless 

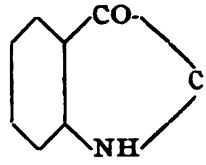
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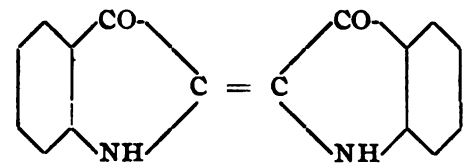
, the CO groups being in the *cis* position since it

[1] Ber., 27, 1726; [2] Ibid., 27, 3527; [3] Ibid., 27, 2530; 30, 75; [4] Ibid., 29, 1075; [5] Ibid., 30, 75; [6] Ibid., 30, 2529; [7] Ibid., 33, 2172; [8] Ibid., 28, 666.

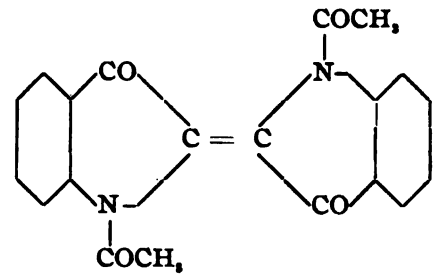
[9] Some weeks ago H. Ley (Z. angew. Chem., 31, 1308) called attention to these differences in color as dependent on configuration in some cases, but did not follow up the matter.

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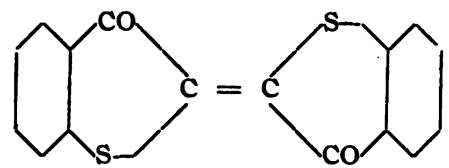
was only possible to obtain a monoxime[1]. There is the possibility of a stereoisomeric indigo which would be formulated  and which would be expected to possess a different color from the ordinary indigo. Some time ago Lieberman and Dickhuth[2] described diacetyl indigo as being red in color. The replacement of hydrogen by an acetyl group does not in general cause such a marked change in color in colored organic compounds, so that the hypothesis may be put forward tentatively that there is a stereoisomeric change here, and that one geometrical isomer is colored blue and the other red. Some of the compounds containing the same chromophoric group as indigo are known and on the above hypothesis would be formulated :—



Indigo (blue)



Diacetylindigo (red)



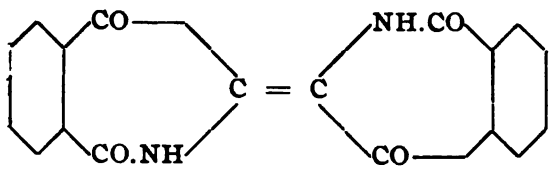
Thioindigo[3] (brownish red)

[1] Thiele and Pickard, Ber., 31, 1252.

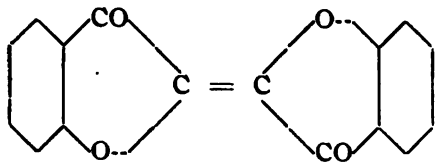
[2] Ber., 24, 4130.

[3] Friedländer, Ann., 351, 390.

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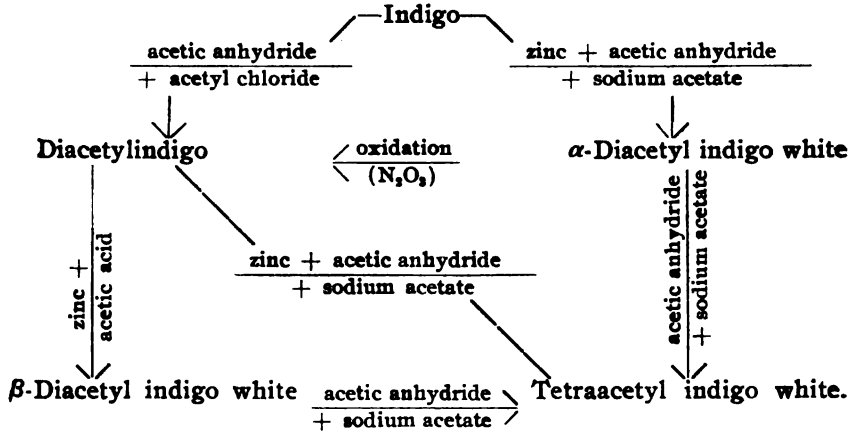
Carbindigo[1] (red)



(red)[2]

Since no further work on diacetyl indigo was published, the subject was taken up at this point. Recently, however, Liebermann and Krauss[3] described some work on similar compounds so that the publication of this preliminary paper was decided upon although the two fields of work do not interfere.

The experimental work of Liebermann and Dickhuth was confirmed in all particulars and some of the relations cleared up. Since all the compounds have been described, only the general scheme of the manner of passing from one to another of these and the reagents best suited for the purpose will be given:—



Owing to their different solubilities in cold alkali Liebermann and Dickhuth ascribe to the two diacetyl indigo whites the groupings —CO—CH—CH—CO— for the α and —C(OH)=C—C=C(OH)— for

[1] Gabriel and Colman, Ber., 33, 996.

[2] Friedländer and Neudörfer, Ber., 30, 1077; 32, 1837.

[3] Ber., 40, 2492.

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the β. They state however that it is impossible to convert one directly into the other. A much more plausible explanation is that the α being prepared from *cis* indigo directly is optically inactive diacetyl indigo white (by internal compensation—similar to mesotartaric acid), whereas the β is prepared from *trans* diacetyl indigo and is therefore a racemic mixture capable of being resolved into its optically active constituents.

The work on indigo is being continued.

LABORATORY OF ORGANIC CHEMISTRY.
September, 1907.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 148.]

EXPERIMENTS UPON BARFOED'S ACID CUPRIC ACETATE SOLUTION AS A MEANS OF DISTINGUISHING GLUCOSE FROM MALTOSE, LACTOSE AND SUCROSE.

BY F. C. HINKEL AND H. C. SHERMAN.

Received October 3, 1907.

In some preliminary work upon the Barfoed test carried out in this laboratory by L. J. Cohen in 1905[1], it appeared to be practicable to distinguish between glucose and maltose in solutions containing less than 0.02 per cent. of the former and at least as much as 0.2 per cent. of the latter, provided the tests are controlled by check experiments with known solutions of the sugars. These results seemed sufficiently favorable to warrant further experiment. The details of the test as used both in Cohen's experiments and in those described below are as follows:

Reagent: Dissolve 45 g. of neutral crystallized cupric acetate in 900 cc. of water, filter if necessary; add 1.2 cc. of 50 per cent. acetic acid and dilute to a liter. A portion of this reagent must show no change when heated in a boiling water-bath for 10 minutes, and on longer heating only a turbidity due to volatilization of acetic acid and formation of basic salt.

Test: To 5 cc. of the reagent in a test tube add the solution to be tested and stand the tube in a water-bath of such depth that the tube is surrounded by boiling water to at least the level of the liquid within. After 3½ minutes remove the tube from the water-bath and examine for cuprous oxide, viewing the tube against a black background in a good light. If no evidence of reduction is found, allow the tube to stand at room temperature for 5 or 10 minutes and examine again. For uniform results the different tubes used in making the tests should be of nearly the same diameter and thickness of wall. It is sometimes advantageous to pour out the liquid at the end of the test, leaving any cuprous oxide as far as possible adhering to the bottom of the test tube and examine again.

[1] Sherman's Methods of Organic Analysis, pp. 75-76.

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Experiments with Known Solutions.

The tests described below were made in order to ascertain the delicacy and reliability of this method for distinguishing glucose from maltose, lactose and sucrose, both in pure solutions and in mixtures.

EXPERIMENTS WITH KNOWN SOLUTIONS.

Sugar tested	Volume of reagent	Volume of sugar solution	Weight of sugar present	Result of 3½ minutes heating
Glucose	5 cc.	1. cc.	0.001 gram.	Distinct reduction
	5 "	0.5 "	0.0005 "	Slight "
	5 "	5. "	0.0002 "	Very slight "
	5 "	10. "	0.0001 "	Doubtful
	5 "	1. "	0.0002 "	Slight reduction
Maltose	5 cc.	4. cc.	0.04 gram.	Slight reduction
	5 "	3. "	0.03 "	" "
	5 "	2.5 "	0.025 "	Very slight "
	5 "	2. "	0.02 "	No reduction[1]
	5 "	1. "	0.025 "	Very slight reduction
	5 "	5. "	0.025 "	" " "
	5 "	10. "	0.025 "	" " "
Lactose	5 cc.	3. cc.	0.03 gram.	Slight reduction
	5 "	2.5 "	0.025 "	Very slight reduction
	5 "	2. "	0.02 "	No reduction[2]
	5 "	1. "	0.025 "	Slight "
	5 "	5. "	0.025 "	Very slight reduction
	5 "	10. "	0.025 "	" " "
Sucrose	5 cc.	3. cc.	0.03 gram.	No reduction[3]
	5 "	1. "	0.025 "	" " [4]
	5 "	5. "	0.025 "	" " [4]
	5 "	10. "	0.025 "	" " [4]

The figures given in the table indicate that when the test is carried out as described, the results depend more largely upon the actual amount of sugar present than upon the volume of water in which the sugar is dissolved.

In this series of tests 0.0002 to 0.0005 g. glucose gave a slight but perceptible reduction under the conditions adopted. Under the same conditions no reductions were observed with 0.02 g. maltose or lactose or with 0.03 g. sucrose. The addition of these amounts of disaccharides to solutions containing known amounts of glucose did not appear to have any marked effect.

Experiments With Unknown Solutions.

As a further test of the method, solutions were prepared by one of us and given to the other for test.

In each case the experimenter was told that the solution submitted contained 1 per cent. of total sugar which might be either a single disac-

[1] Very slight reduction on heating for 6 minutes.
[2] Slight reduction on heating for 6 minutes.
[3] Slight reduction on heating for 6 minutes.
[4] Slight reduction on heating for 8 minutes.

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charide or a mixture of disaccharide and glucose, and was requested to decide (by means of the test above) which of the samples contained glucose and to arrange them in order of the amount present. These experiments upon unknown solutions, mostly mixtures, gave the following results:

Solutions Containing Sucrose. Five solutions were prepared containing respectively (1) Sucrose 0.96 per cent.; glucose 0.04 per cent. (2) Sucrose 0.97 per cent.; glucose 0.03 per cent. (3) Sucrose 0.98 per cent.; glucose 0.02 per cent. (4) Sucrose 0.99 per cent.; glucose 0.01 per cent. (5) Sucrose 1.0 per cent.; glucose, none.

The experimenter, knowing only that the total sugar was in each case 1 per cent. of the solution, used only 2 cc. (containing 0.02 g. total sugar) for each test, so as to avoid appreciable reduction due to disaccharide alone. The first three solutions were found to contain glucose and were arranged correctly with reference to the amounts present.

Solutions Containing Lactose. Five samples parallel with those just described, but containing lactose instead of sucrose were prepared and tested in the same manner and with the same results.

Solutions Containing Maltose. These were also prepared and tested in the same way as the solutions containing sucrose and again no glucose was found when only 0.0002 g. was present but the other tubes all showed reduction and were correctly arranged in order of glucose content.

With known solutions containing glucose only, it seemed possible to note an effect upon the reagent when only 0.0002 g. glucose was present, whereas in each of the three sets of unknown solutions containing disaccharides the limit of delicacy of the test seemed to be reached at about 0.0004 g. It is not believed that this apparent discrepancy indicates an interference due to the disaccharide,[1] but rather that a very minute reduction which was accepted as a positive test in known glucose solutions where other sugars were absent, did not appear sufficiently convincing in unknown solutions where relatively large amounts of a disaccharide were presumably present.

Thus in unknown solutions containing approximately 1 per cent. (0.02 gram.) of either sucrose, lactose or maltose, the test sufficed to distinguish the presence of 0.02 per cent. (0.0004 gram.) of glucose and to show differences of 0.01 per cent. The test has also been found useful in the detection of glucose in the presence of nine times its weight of a mixture containing the three disaccharides mentioned.

Experiments Upon Complete Destruction of Glucose.

Since it has been proposed to detect glucose in sugar mixtures by means of Barfoed solution and then use the filtrate for the detection of maltose or lactose[2], it becomes important to know, not only the minimum amount

[1] Such as the interference of maltose and lactose with the osazone test for glucose, this Journal, 28, 629.

[2] Bartley and Mayer, Merck's Report, 12, 100 (1903).

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of glucose which can be detected, but also the maximum amount which will be completely destroyed, since presence of undestroyed glucose would obviously render useless any reduction tests for maltose or lactose in the filtrate.

In the experiments upon this point, known amounts of glucose each contained in 5 cc. of water, were treated with 5 cc. of the reagent as above described and after 3½ minutes heating were filtered, the filtration repeated if necessary, until a clear filtrate was obtained and this was then boiled gently for 2 minutes over a free flame. This was repeated with diminishing amounts of glucose until the two minutes boiling of the acid filtrate showed no further reduction, but when such a filtrate was mixed with Fehling's alkaline tartrate solution before boiling a reduction occured indicating incomplete destruction of the glucose by the Barfoed solution. The tests were continued to find how much glucose would be so completely destroyed by the Barfoed solution as here used, that the filtrate would give no evidence of reducing sugar on mixing with alkaline tartrate and boiling for 2 minutes. This amount of glucose was found to be 0.0025 to 0.003 gram. Hence it appears that if the Barfoed test be used as part of a general scheme for sugar mixtures in the manner proposed by Bartley and Mayer, the amount of glucose (or of total monosaccharide calculated as glucose) present in the portion of solutiont ested, should not exceed 2 milligrams for 5 cc. of the acid cupric acetate reagent.

Conclusions.

On account of the difficulty of securing an exact degree of acidity in the cupric acetate solution, each chemist should demonstrate the efficiency of his reagent, as well as verify his manipulation, by check experiments upon known sugar solutions covering the probable range of composition of the unknown solutions to be tested.

As here described the test was efficient for the detection of 0.0004 gram. of glucose, either alone or in the presence of maltose, lactose or sucrose up to 0.02 gram.

Reduction due to disaccharide occurs if too much either of sugar or of acid be present, or if the heating be too prolonged.

In order to effect complete destruction of the glucose, so that the filtrate might be utilized in testing for maltose or lactose, it was necessary to limit the amount to about 0.002 gram of glucose to 5 cc. of the reagent.

It appears that the test requires very careful regulation as to details of manipulation and amount of sugar tested, but under such restrictions is capable of greater usefulness than has generally been appreciated.

A TRIAL OF THE POLARISCOPIC METHOD FOR THE DETERMINATION OF GLIADIN.

By G. W. Shaw.

Received October 10, 1907.

In Vol. XXVI, No. 3, of this Journal, Professor Harry Snyder suggested the use of the polariscope for the determination of gliadin in our

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as offering a method which would reduce the time required by the ordinary Gunning-Kjeldahl operation, and at the same time be sufficiently accurate for technical purposes.

In connection with a line of cereal investigations now under way at the California Experiment Station the writer recently made some comparative trials of this method against the ordinary procedure. Inasmuch as the range of materials covered in these trials was somewhat different from those mentioned in the original article by Prof. Snyder, the results are set forth below:

Laboratory No.	Gliadin Nitrogen Calculated to Dry Matter. By Polariscope Method.	By Gunning Method.	Difference
19	0.72	—	—
249	0.56	0.54	+. 02
254	0.46	0.49	— .03
257	0.38	0.40	— .02
265	0.42	0.43	— .01
266	0.42	0.44	— .02
268	0.39	0.39	— .00
270	0.38	0.43	— .05
288	0.49	0.49	.00
290	0.57	0.64	— .07
313	0.39	0.55 (?)	— .16
322	0.39	0.53 (?)	— .14
326	0.49	0.50	— .11

The above determinations were made upon soft white wheat meals. In this lot of samples the gliadin determination by the Gunning method had already been made several weeks before the trial of the polariscope method.

Determinations were made by the polariscopic method on the basis of the changed moisture content of the sample, and the results in each case calculated to dry matter for comparison. Further, the methods were operated by different parties, so there were undoubtedly introduced into the operation greater differences in the manipulation of securing solution of the gliadin than if the two operations had been conducted by the same person. Notwithstanding these sources of error it will be noted, that with the exception of Nos. 313 and 322, concerning which there was previouly existing some doubt as to the accuracy of the original determination, the polariscopic method gave results which are within the range of error of most operations.

The above results not being quite satisfactory, the comparison of methods was carried further with the same class of material, the sample operated upon in the one method being taken from the same solution as in the other, one portion being used for polarization and another treated by the Gunning method. The solution of gliadin in these trials was effected by digesting in the cold, as described by Snyder, 15.97 grams of the

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material in 100 cc. of 70 per cent. alcohol. The flask was shaken at intervals of half an hour for two hours, and left overnight before filtration. Ten cubic centimeters of this solution were used for treatment by the Gunning method, after first driving off the alcohol by evaporation. By this procedure one would expect somewhat closer results than by the former.

SOFT WHEATS.

By Polariscope Method.	By Gunning Method.	Difference.
0.90	0.91	— .01
0.70	.069	+ .01
0.86	0.90	— .04
0.81	0.75	+ .06
0.64	0.63	+ .01
0.70	0.70	.00
0.66	0.69	— .03
0.92	0.94	— 0.2
0.64	0.69	— .05
0.95	0.94	+ .01
0.57	0.59	— .02
0.55	0.60	— .05
0.73	0.71	+ .02
0.62	0.60	+ .02
0.62	0.66	— .04
0.53	0.56	— .03
0.90	0.92	— .02
0.88	0.85	+ .03
0.81	0.78	+ .03
0.70	0.70	.00
0.73	0.74	— .01
0.77	0.78	+ .01
0.62	0.60	+ .02
0.59	0.57	+ .02
0.64	0.60	+ .04
0.64	0.60	+ .04
0.55	0.58	— .03
	Average Difference,	—0.03
	FLOUR.	
0.77	0.75	+ .02
0.59	0.57	+ .02
0.51	0.48	+ .03
0.46	0.43	+ .03
0.62	0.55	+ .07
0.77	0.70	+ .07
0.86	0.84	+ .03
	Average Difference,	+0.04
	DURUM WHEATS.	
0.84	0.83	+ .01
0.77	0.78	— .01
0.95	0.94	+ .01
0.70	0.76	— .06
0.66	0.69	— .03
0.75	0.75	.00
0.79	0.83	— .04
0.59	0.62	— .04
0.81	0.78	+ .03
0.64	0.64	.00
	Average Difference,	—0.02

NOTE: Credit should be given Messrs. E. J. Lea and B. R. Jacobs for the routine work connected with these determinations.

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It will be noted that in but three cases out of the forty-five last stated does the difference between the two methods exceed 0.05, which is certainly as close as one can expect ordinary technical work to be done, and as between two samples is undoubtedly within the limits of accuracy of sampling large lots.

A still further test of the method was given by making a gliadin determination upon a gluten flour in which the Kjeldahl method showed 3.32 per cent. of gliadin nitrogen. The polariscopic method showed 3.45 per cent.

Considerable difficulty was experienced at the outset in securing a clean solution for filtration, but this was finally overcome by avoiding excessive agitation.

Snyder remarks that in the case of flours analyzed by him, and probably grown in the middle west, " the combined alcohol soluble carbohydrates and non-gliadin proteins of the alcoholic solution affect the polarization to only a slight extent," and states that after the gliadin protein was precipitated the non-gliadin rotary bodies showed a reading of less than 0.20 on the sugar scale.

In our experience with the method it was always found necessary to make two polarization determinations, the first of the original solution, and the second after separating the protein bodies by the use of a concentrated solution of mercuric nitrate, and then making the required correction to give the true gliadin reading.

This was particularly true in the case of wheat meals where the average difference between the two polariscope readings was 1.05 on the sugar scale corresponding to 0.21 per cent. on the gliadin scale, the range of differences on the sugar scale being from 0.08 to 2.75. In the case of flours, unless extreme accuracy is required, the correction could be neglected inasmuch as the error is much less, not exceeding 0.04 per cent. of the gliadin scale.

The writer is strongly impressed with the idea that the method is worthy of a much more extended use than it has so far had, and that if precautions are taken to correct for the effect of other optically active bodies, there are fewer opportunities for error than with the ordinary method of nitrogen determination.

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THE SOLUBILITY OF STEARIC ACID IN ETHYL ALCOHOL AT ZERO.

By W. H. EMERSON.

Received August 14, 1907.

In some work on the determination of stearic acid by the method of Hehner and Mitchell,[1] difficulty was experienced in obtaining a definite

[1] Analyst, 21, 316; also This Journal, 19, 32 (1897) and Lewkowitsch, Oils, Fats and Waxes, 3rd edition, p. 355.

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saturated solution of stearic acid. As the preparation of a solution which shall be saturated under the conditions of the determination is essential to the accuracy of the method, it was decided to study the solubility of stearic acid in ethyl alcohol at 0°.

Kreis and Hafner found[1] the solubilities of both stearic and palmitic acids much lower than had been previously given by Hehner and Mitchell. They also found that small amounts of stearic acid, below about 0.1 grm., form highly supersaturated solutions, and that very small amounts will not crystallize at all from a saturated solution, even though treated with a crystal of the acid and allowed to stand indefinitely, a fact with which I had also met.

The first step in the work was the preparation of a pure stearic acid. The melting point of the acid has been variously given from 68.5° to 71.5°. As a starting point a special stearic acid from Kahlbaum was used. The melting point was determined carefully using a thermometer standardized at the Reichsanstalt, graduated to 1/5°, and the usual small melting tubes. The melting point was found 66.6°-68.3° (corr.). The range was observed from the first indication of change, marked by a shrinking of the test, to complete liquefaction, with very slow rise in temperature, about 0.1° per minute. The acid was then crystallized repeatedly from alcohol of about 95 per cent., noting the melting point from time to time. At the eighth crystallization it melted at 69.1°-69.4° (corr.) and further crystallization did not raise the melting point. Slight fluctuations of temperature due to irregularity of stirring were observed. This melting point agrees best with that of de Visser, 69.32°.

The alcohol used was the "95 per cent." alcohol of commerce distilled from potassium hydroxide, 50 cc. left 0.2 mg. residue on evaporation. The specific gravities were determined by weighing in a picnometer provided with a thermometer and capillary side tube. The weighings were reduced to a vacuum. Essentially the same apparatus was used as recommended by Hehner and Mitchell in determining stearic acid except that one limb of the filtering tube was prolonged so as to form a siphon. To prevent unnecessary access of atmospheric moisture, which it was feared might condense in the cold flask and cause dilution of the alcohol, the crystallizing and receiving flasks were closed with two hole rubber stoppers, the siphoning apparatus passing through one hole in each, and the other closed by capillary (thermometer) tubing. The method of procedure was generally to dissolve the acid in 100 cc. of alcohol in a tightly stoppered flask, place both in the ice over night, shake in the morning, allow to stand four hours in the ice, then siphon off, using the pump to start the siphon. The alcoholic solution was then weighed, evaporated, and from the weight of the residue the solubility determined. The residue

[1] Z. Unters. Nahrungs und Genussm., Jan., 1903.

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in the crystallizing flask was dissolved again, followed by recrystallization in the ice bath, filtration, etc. This was repeated as often as desired. After the first solution, 50 cc. was generally used for resolution—sometimes 100 cc. throughout.

Some preliminary experiments showed that the solubility remained nearly constant as long as a considerable excess of stearic acid was present.

The following series was made with alcohol, specific gravity 0.81577, at 14.7°—about 95.1 per cent. by volume. Two tests were made at the same time and the table gives the parallel and successive solubilities expressed in grms. per 100 cc. at 0°.

TABLE 1.

Stearic Acid. 0.793 grms. Solubility	Vol. Alcoho	Stearic Acid. 0.775 grms. Solubility
a 0.1135	100 cc.	a′ 0.1144
b 0.1139	50 "	b′ 0.1134
c 0.1158	" "	c′ 0.1213
d 0.1164	" "	d′ 0.1164
e 0.1215	" "	e′ 0.1221
f 0.1241	" "	f′ 0.1257
g 0.1339	" "	g′ 0.1408

Previous to the solution for the test *c′*, the residual alcohol of the preceding test, (between 5 and 10 cc.) had been evaporated on the water bath.

At the test *e*, where the solubility began to increase rapidly it was estimated by weighing the residue and calculating back that 0.45 grm. of acid was present, and at *e′* 0.43 grm. The exact amount could not be determined owing to uncertainty as to the loss due to solution remaining in the tube, and acid adhering to the filtering tube. These results indicate that supersaturation occurs with a much larger amount of acid present than was found by Kreis and Hafner.

The next series was made to try the effect of varying several conditions. Alcohol—specific gravity 0.80706 at 22.2°, about 95.7 per cent. by volume.

TABLE 2.

Stearic Acid. 0.742 grms. Solubility	Volume of Alcohol	Stearic Acid. 0.699 grms. Solubility
a 0.1234	100 cc.	a′ 0.1251
b 0.1250	50 "	b′ 0.1280
c 0.1282	" "	c′ 0.1284
d 0.1242	" "	d′ 0.1253
e 0.1280	" "	e′ 0.1309
	" "	f′ 0.1427

For *b*, the residual alcohol of the previous test was evaporated over sulphuric acid in a vacuum desiccator, and the acid redissolved without heating. For *b′*, the residual alcohol was evaporated on the steam bath,

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and the acid redissolved without heat. For c and c', the alcohol was evaporated on the steam bath, and for c redissolved with a small flame and for c' on the steam bath. In redissolving with heat the solution as a whole was not allowed to become appreciably warm to the hand.

Apparently the only factor, other than the amount of acid, which appreciably affected the solubility was evaporation on the steam bath with alcohol. The amounts of acid present at e and e', when the solubility began to rise, were estimated to be 0.43 grm. and 0.39 grm. respectively.

The next test was made to see if supersaturation set in with a larger amount of acid present, when using a larger volume of alcohol, so 100 cc. was used throughout. It had been found that 0.7 grm. did not give a supersaturated solution with 100 cc. alcohol.

Alcohol, 0.80766 at 22.1°—about 95.5 per cent.

TABLE 3.

Stearic Acid. 0.782 grms. Solubility	Vol. Alcohol	Stearic Acid. 0.711 grms. Solubility
a 0.1217	100 cc.	a′ 0.1229
b 0.1268	"	b′ 0.1296
c 0.1462	"	c′ 0.1516

Supersaturation set in for b with 0.64 grm. acid present and b' with 0.57 grm. c' was allowed to stay in the ice bath over 40 hrs. with occasional shaking, which did not apparently overcome the supersaturation to any extent.

There was some evidence that supersaturation set in later, *i. e.* with a smaller amount of acid present with more dilute alcohol—so the following test was made:

Alcohol, 0.80869 at 25.6°—about 94.5 per cent.

TABLE 4.

Stearic Acid. 0.525 grms. Solubility	Vol. Alcohol	Stearic Acid. 0.429 grms. Solubility
a 0.1037	50 cc.	a′ 0.1033
b 0.1052	"	b′ 0.1073
c 0.1083	"	c′ 0.1144

For c and b' the amounts of acid were 0.39 and 0.36 respectively. Comparing with Table 2 we see that the difference is slight if any, with this variation in specific gravity—c' was allowed to stand for over 40 hrs. in the ice bath with occasional shaking.

In the preceding determinations, while the solubilities were nearly constant with stearic acid above a certain amount, yet a slight irregular increase is noticeable. It was thought that this might be due to evaporating the succeeding solutions in the flask with the stearic acid from the preceding determinations. Some trials showed that there was a slight increase in weight on evaporating stearic acid with alcohol.

In order to determine if there is a slight increase in solubility, preced-

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ing the rapid increase supposed to be due to supersaturation, the following test was made:—

Alcohol, 0.81228 at 22.2°—about 94.3 per cent.

TABLE 5.

Stearic Acid	Vol. Alcohol	Solubility
2.09	100	0.0954
1.89	"	0.0986
1.4	"	0.1001
0.97	"	0.0996

The first three results suggest a progressive increase in solubility. On the other hand there is only a variation of about 1 per cent. in solubility between the 2nd and 4th tests with a variation of 1 grm. of acid, and this variation is probably within the limits of error of the determinations. For use in Hehner and Mitchell's method, therefore, the solubility may be considered as practically constant for quite a wide range in the amount of stearic acid, when above about 0.7 grm. using 100 cc. of alcohol of 94 to 95 per cent., and when above about 0.5 grm. using 50 cc. of alcohol.

The solubilities found within this range and already given are here summarized :—

TABLE 6.

Specific gravity of alcohol at 0°	Approximate strength of alcohol by volume	Amount dissolved in 100 cc. at 0°
0.82650	95.7%	0.1246 grms.
0.82715	95.5	0.1223 "
0.82871	95.1	0.1139 "
0.83126	94.5	0.1035 "
0.83183	94.3	0.0996 "

The specific gravities were reduced to 0° assuming 0.00088 as the change of specific gravity per degree. The solubility was determined as already stated by evaporating the alcohol and weighing the residue, and as this gives a slight increase in weight to the acid, the above values should be somewhat too high. This error is however of little importance as the other errors of the determination are much larger, probably about 1 per cent. Hehner and Mitchell found the solubility to be 0.15 grm. in 100 cc. of 94.4 per cent. alcohol. Kreis and Hafner found a much lower value 0.1249 in 95 per cent. alcohol. Calculations from the results above, give 0.1123 grm. as the solubility, in 95 per cent. alcohol, about 10 per cent. lower than the result of Kreis and Hafner. If they were using about 0.5 grm. in their solubility determinations, as seems probable from their article, then the explanation of the difference might be that they were working just within the range of supersaturation. The rather wide variations in their individual results, 0.1220 to 0.1310, would also imply this.

Hehner and Mitchell give the weights of acid used in their solubility determinations as 0.2 to 0.5 grm. per 100 cc. of alcohol. Their value for the solubility should therefore have been too high, as seems to have been

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the case. At the same time they found nearly identical values for the varying amounts of acid, which does not agree with the results presented above, as, under the conditions given, there was invariably a steady increase in solubility after the acid had fallen below about 0.7 grm. using 100 cc. alcohol.

Some further tests were made bearing on the increased solubility due to evaporation with alcohol.

1.272 grms. of the acid were evaporated on the steam bath with 50 cc. of 94.3 per cent. alcohol which had been distilled from potassium hydroxide. The solubility was then determined using 100 cc. and found to be 0.1196 grm. The normal solubility for this alcohol was about 0.1000 grm., deducting this from that found, leaves 0.0196 grm. excess soluble matter, or 1.54 per cent. of the acid used.

Since the lower fatty acids in general give esters when heated with alcohol, it was perhaps to have been expected that ethyl stearate would be formed here, thus increasing the apparent solubility. However, considering the high molecular weight of the acid, the brief time of the action, and the hydrolysis due to the considerable proportion of water, this was thought at least doubtful. Another possible explanation of the increased solubility was that the alcohol contained some foreign substance of a basic nature, perhaps alkaloids. Some alcohol was therefore prepared by distillation from stearic acid, followed by distillation with potassium hydroxide and again with stearic acid. 1.713 grms. of acid were evaporated with 50 cc. of this alcohol and the solubility determined. The result showed an excess solubility of 0.0245 grm. per 100 cc. or 1.43 per cent. of the acid used, differing but little from the above. If due to the ester, it was thought that its amount would be increased by evaporating with absolute alcohol, thus partly avoiding the hydrolytic action of the water. So 1.048 grm. of acid were evaporated with 50 cc. of a 99 per cent. alcohol. The excess solubility was 0.0132 grm., 1.26 per cent. of the acid used—somewhat less than with alcohol of 94.3 per cent. Evaporation with 80 per cent. alcohol gave an excess of 1.1 per cent. of the acid. Finally a solution of the acid in alcohol was allowed to stand five days at temperatures mostly from 25° to 30° and the solubility determined in comparison with a freshly dissolved sample under otherwise identical conditions. The former showed a solubility of 0.1007, the latter 0.0983—a difference somewhat more than the probable error of experiment.

So far as could be ascertained from the literature available the formation of the ester under these conditions had not been noted, and it is intended to investigate this point further.

From the above it appears that in order to determine small amounts of stearic acid accurately it will be necessary to add a weighed amount of

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pure acid sufficient to bring the total up to about 0.7 g. for 100 cc. of alcohol or 0.5 grm. for 50 cc. of alcohol. The "saturated" solution used can be tested for supersaturation by evaporating a portion of it and comparing with the solubilities of Table 6, provided the acid has been treated so as to avoid the action of the alcohol on it. It would seem necessary also to keep in mind this action between the alcohol and acid in determining stearic acid in mixtures which have been recovered from alcoholic solution. W. H. EMERSON.

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[CONTRIBUTION FROM BUREAU OF ANIMAL INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE].

THE APPLICATION TO SOLID FATS OF RENARD'S TEST FOR PEANUT OIL.

BY W. B. SMITH.

Received October 4, 1907.

Tolman's modification of Renard's test for peanut oil[1] is the best method in use for the purpose and is generally employed in testing edible oils for adulteration. Briefly this method is carried out as follows: The sample is saponified with alcoholic potash and treated with lead acetate, the lead soap being treated with ether, which dissolves the lead oleate, linoleate, etc. leaving the lead stearate, palmitate and arachidate as a residue. The precipitate is treated with hydrochloric acid and the liberated fatty acids freed, separated and dried. They are then dissolved in 90 per cent. alcohol and cooled to 15°, when the arachidic acid crystallizes out, is weighed and the melting point taken. Twenty times the amount of arachidic acid gives the approximate amount of peanut oil present.

In connection with this method, however, Tolman and Munson say[2] "Twenty grams of the oil to be tested should be taken so that enough of the arachidic acid can be separated to make the melting point which should be determined in every case, as some oils, such as cottonseed and lard, will give a precipitate which resembles arachidic acid except that it has a lower melting point."

In working with mixtures of solid fats with cottonseed oil, the writer, in nearly every case in which a test was made has obtained a precipitate at the point where arachidic acid should come down, although this precipitate was very often gelatinous in appearance, whereas the arachidic acid is crystalline.

The following table shows comparative results obtained with oleostearin,

[1] Bulletin 65, Bureau of Chemistry, U. S. Department of Agriculture.

[2] Olive Oil and its Substitutes; Bulletin 77, Bureau of Chemistry, U. S. Department of Agriculture, p. 35.

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lard, and the same lard with 10 per cent. peanut oil admixed. Determinations made on pure peanut oil are added for comparison.

	% solid acids	% crystallizing from 90% alcohol	% remaining in solution	Beginning of crystallization	Iodine number of crystals	Melting point of crystals
Peanut oil	13.73	4.24	9.49	37°	0.7	71.5
Lard	39.30	5.93	33.37	20°	7.4	54.3
Lard plus 10% peanut oil..	37.35	1.62	35.73	19°	4.2	55.0
Oleostearin	36.31	15.18	20.98	25°	4.9	61.5

The amount of solid acids in oleostearin and lard crystallizing at 15° from 90 per cent. alcohol is far greater than in peanut oil, although the temperature at which crystallization begins is far lower. The cause of the precipitation, while primarily, of course, the same as that of arachidic acid, *viz.* the supersaturation of the solution, differs in this, that the arachidic acid precipitates because of its very slight solubility in 90 per cent. alcohol, while the other acids come down because of the great quantity of them in the solution, as shown by the amount remaining in solution after crystallization.

As shown by the table, the melting points of the crystals from the pure lard and those from the lard containing 10 per cent. of peanut oil were about the same and hence not conclusive. The crystals were therefore redissolved in 90 per cent. alcohol and allowed to recrystallize. The melting points were again determined and found to be, pure lard 55°, lard with 10 per cent. peanut oil 77°, showing that nearly pure arachidic acid had been obtained in the latter case.

These results show that the addition of fats containing large percentages of solid fatty acids to cottonseed oil or other oils interferes materially with the detection of peanut oil by this method, and in case the presence of peanut oil is suspected in such mixtures, some modification of the method will be necessary to detect it; either to increase the proportion of 90 per cent. alcohol used, which would be objectionable, or to recrystallize the "arachidic acid" until a melting point higher than that of stearic acid is obtained, when the presence of arachidic acid is established.

SOUTH OMAHA, NEB.,
Aug. 9, 1907.

THE OCCURRENCE OF NITRATES IN VEGETABLE FOODS, IN CURED MEATS AND ELSEWHERE.

BY W. D. RICHARDSON.
Received October 9, 1907.

For the purpose of this paper the term "vegetable foods" is used so as to include fruits.

The presence and amount of nitrates in vegetable foods has been noted and determined by Frühling and Grouven, by Sutter and Alwens, by E. Schultze and H. Schultze and others[1]. Frühling and Grouven state

[1] Koenig, Nahrungs und Genussmittel, Vol. 2, p. 94-95.

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that nitric acid is not present in ripe seeds, but in green plants of the Gramineae and Leguminosae they found as much as 0.10 per cent. Sutter and Alwens working on beets found quantities up to 3.49 per cent. nitric acid in the dry substance. E. Schultze and H. Schultze report in beet juice from 0.13 per cent. to 0.285 per cent. nitric acid; E. Schultze and A. Ultrich in beets 0.41 to 0.407 per cent. The same authors report, that of the nitrogen in beets, 32.51 per cent., or nearly one-third the total, exists in the form of nitric acid. Sugar beets contain according to Zoller, 0.324 to 0 926 per cent. nitric acid.[1] E. Egger states that grapes contain no nitrates[2]. Hence the deduction has been made that the presence of nitrates in wine indicates watering of this product. On the other hand Spica[3] finds nitrates occurring naturally in certain musts, and hence concludes that their presence does not necessarily indicate adulteration. Schönbein reports nitric acid present in beer and wine up to 4 to 10 mg. per liter.

The results of the investigations carried out in this laboratory and detailed below, indicate a more general distribution and the presence of larger quantities of nitric nitrogen in vegetable foods than has been commonly supposed. Inasmuch as nearly all of the nitrogen demanded by plants for their growth is taken from the soil in the form of nitrates —a smaller quantity being absorbed possibly as ammonium salts—it is logical to infer that, especially in the earlier stages of growth, significant amounts of nitrates should be found in the plant organism. It would seem reasonable too, to conclude that as the plant develops and approaches maturity, elaborating the nitrate nitrogen into the form of protein bodies, smaller quantities should be found. In other words, as would be expected of a substance which enters at once into metabolic process and is at once changed thereby, the quantities of nitrates found should vary greatly, and the smallest quantities should occur in the mature plants. This seems generally to be the case. The surprising fact is, however, that in certain crops, particularly beets, considerable quantities occur in the fully matured plants. Even in ripe seeds and mature fruits the presence of nitrates has been established qualitatively and quantitatively in practically all samples analyzed. This is the more astonishing in the case of fruits inasmuch as during the ripening process the nitrates must be in contact with many reducing substances.

The presence of nitrites has also been established in a number of vegetable foods, and it seems that here as elsewhere in nature where nitrates occur, nitrites may reasonably be expected. In celery, lettuce, turnips, radishes and beets, quantitative determinations of nitrites were

[1] Koenig, Nahrungs und Genussmittel, 4th Ed., Vol. 2, p. 94-95.
[2] Chem. Centr., 1885, 71-72.
[3] Gazz. chim. ital., 1907, 37; ii. 17-22.

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made by a colorimetric method employing Griess' solution of alpha naphthylamine and sulphanilic acid in acetic acid, with the following results:

		Nitrites in Vegetable Foods.		Dry Basis	
Sample.	Moisture.	Nitrite Nitrogen.	Equivalent to Potassium Nitrite.	Nitrite Nitrogen.	Equivalent to Potassium Nitrate.
Celery,	94.3%	0.001 %	0.0044 %	0.0173%	0.0772 %
Lettuce,	76.4	0.0023	0.0109	0.0097	0.0461
Turnips,	86.4	0.00013	0.00058	0.00095	0.0004
Radish,	93.6	0.0023	0.0109	0.035	0.170
Beets,	92.1	0.0018	0.0088	0.0227	0.114

The question whether the nitrites contained in vegetables are absorbed as such from the soil or whether they are produced from nitrates by reduction processes occurring in the plant was not entered into. The general occurrence of nitrites in soils and surface waters would indicate the possibility of their entering the plant from these sources. The writer has observed that beef cut in small cubes and stewed with fresh vegetables such as string beans, tomatoes, potatoes and onions, assumes the color of nitrosohemochromogen, thus indicating the presence of nitrites in the same way as when fresh beef is boiled with saltpeter-cured bacon or a dilute solution of nitrite itself.

In the following investigations the vegetables and fruits used were purchased in the open market during the month of September, some being obtained from wholesale and some from retail dealers. Because vegetables in the Chicago market in some instances come from a considerable distance, it was not possible in every case to obtain them in as fresh condition as desirable and this might lead to low results. The analyses were made as promptly as possible after the arrival of the sample at the laboratory, inasmuch as it is probable that the nitrates present would gradually be reduced as the sample grew stale and withered.

The Schloesing-Wagner method was used for all determinations, 100 grams being the quantity of substance used. Water was the extracting medium except in those cases where the presence of large quantities of starch precluded its use and then a mixture of equal quantities of alcohol and water was used. When working on 100 grams of material one cc. of nitric oxide is the equivalent of about 0.004 grams saltpeter or 0.004 per cent. and the method will detect as little as one or two-tenths of this quantity or 0.0004 per cent. to 0.0008 per cent. Nearly all doubtfully small quantities were checked qualitatively by a test with diphenylamine and sulphuric acid working on an extract of the original substance, or with potassium iodide and starch solution working on the nitric oxide liberated in the determination, by sucking the nitric oxide through the test solution contained in a test tube fitted with long inlet-

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and short outlet-tubes and closed by a doubly perforated rubber stopper. This method was found to be very sensitive.

For the analytical work shown in the following tables the writer is indebted to Messrs. Scherubel, Morgan, Hansen, Lehnert, Berry, Winkley, Heath and Hale and Miss Wishart of this laboratory.

TABLE A.

NITRATES IN VEGETABLE FOODS ARRANGED IN THE ORDER OF MAXIMUM QUANTITIES FOUND.

Food	Sample No.	Moisture %	Nitrate Nitrogen %	Equivalent to Saltpeter %	Dry Basis: Nitrate Nitrogen %	Dry Basis: Saltpeter %
Beet	1	75.1	0.182	1.327	0.731	5.33
	2	90.4	0.067	0.469	0.767	5.45
	3	76.4	0.059	0.431	0.230	1.66
	4	74.3	0.034	0.249	0.137	0.99
	5	77.3	0.027	0.200	0.119	0.97
	6	65.3	0.021	0.170	0.061	0.49
	7	92.1	0.021	0.170	0.263	1.91
Egg Plant	1	92.2	0.100	0.801	1.287	10.27
	2	93.5	0.015	0.102	0.228	1.57
	3	92.9	0.011	0.080	0.155	1.13
	4	94.0	0.008	0.062	0.142	1.03
Spinach	1	90.3	0.086	0.624	0.890	6.46
	2	90.2	0.049	0.360	0.557	4 09
	3	90.1	0.042	0.307	0.427	3.13
	4	90.3	0.033	0.240	0.341	2.48
	5	89.7	0.007	0.051	0.068	0.49
Lettuce	1	92.2	0.080	0.580	1.025	7.44
	2	76.4	0.048	0.347	0.187	1.36
	3	93.0	0.028	0.210	0.400	3.00
	4	74.7	0.024	0.190	0.102	0.75
	5	92.3	0.009	0.071	0.143	1.05
Radish	1	93.2	0.069	0.500	1.020	7.41
	2	95.3	0.050	0.369	1.006	7.85
	3	95.2	0.041	0.300	0.861	6.31
	4	93.9	0.039	0.289	0.638	4.74
	5	95.4	0.037	0.266	0.798	5.78
	6	93.2	0.012	0.103	0.178	1.51
Celery	1	95.8	0.065	0.476	1.559	11.32
	2	94.5	0.034	0.245	0.637	4.62
	3	94.2	0.029	0.200	0.509	3.51
	4	90.6	0.024	0.180	0.307	1.91
	5	94.3	0.018	0.129	0.481	3.50
Turnip	1	91.0	0.065	0.470	0.721	5.21
	2	79.2	0.035	0.256	0.168	1.23
	3	91.7	0.011	0.090	0.134	1.08
	4	85.9	0.005	0.039	0.038	0.28
	5	86.1	0.002	0.017	0.017	0.13
Canned Spinach	1	91.3	0.044	0.322	0.487	3.70
	2	91.4	0.030	0.218	0.350	2.54

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Food	Sample No.	Moisture %	Nitrate Nitrogen %	Equivalent to Saltpeter %	Dry Basis: Nitrate Nitrogen %	Dry Basis: Saltpeter %
Canned Spinach	3	92.9	0.025	0.179	0.348	2.51
	4	91.7	0.024	0.176	0.290	2.15
	5	92.3	0.006	0.048	0.074	0.63
Parsley	1	64.1	0.032	0.241	0.125	0.93
	2	82.7	0.017	0.123	0.098	0.71
Summer Squash	1	96.7	0.031	0.225	0.939	6.82
	2	94.6	0.015	0.106	0.270	1.96
	3	96.7	0.010	0.072	0.303	2.18
	4	94.6	0.007	0.052	0.131	0.96
Onion	1	90.7	0.019	0.139	0.205	1.50
	2	86.9	0.0008	0.006	0.006	0.046
	3	76.4	0.0005	0.0038	0.002	0.016
	4	73.0	0.0004	0.003	0.001	0.011
String Beans	1	92.2	0.015	0.109	0.192	1.40
	2	90.6	0.014	0.104	0.169	1.23
	3	91.5	0.010	0.079	0.117	0.93
	4	91.1	0.001	0.009	0.013	0.10
Cucumbers	1	95.0	0.012	0.088	0.240	1.76
	2	97.3	0.002	0.017	0.085	0.63
	3	96.3	0.002	0.014	0.051	0.38
	4	96.1	0.001	0.013	0.035	0.32
	5	96.7	0.001	0.007	0.027	0.21
Leek	1	89.1	0.011	0.080	0.102	0.73
	2	87.7	0.009	0.064	0.075	0.52
Cabbage	1	93.0	0.011	0.078	0.153	1.11
	2	81.6	0.005	0.036	0.031	0.22
	3	91.6	0.004	0.029	0.046	0.34
	4	82.3	0.002	0.014	0.010	0.75
	5	93.1	0.0008	0.006	0.016	0.09
Cauliflower	1	90.2	0.009	0.064	0.090	0.65
	2	89.9	0.0006	0.004	0.006	0.036
	3	88.9	0.0006	0.004	0.006	0.036
Beans (Navy)	1	12.9	0.002	0.016	0.002	0.018
	2	13.5	0.0011	0.008	0.0014	0.010
" Kidney	3	20.0	0.0004	0.003	0.0005	0.004
" Lima	4	17.2	0.007	0.048	0.0084	0.058
Canned Pumpkin	1	91.2	0.006	0.042	0.066	0.478
German Celery	1	90.0	0.005	0.036	0.049	0.360
	2	89.9	0.004	0.030	0.041	0.297
Canned Kidney Beans	1	76.0	0.004	0.030	0.016	0.119
	2	74.4	0.0008	0.006	0.003	0.023
Bread	1	32.6	0.0009	0.007	0.001	0.010
	2	33.2	0.0006	0.005	0.0009	0.016
Tomato	1	93.8	0.002	0.0147	0.034	0.237
	2	94.2	0.0017	0.0128	0.025	0.188
	3	94.3	0.0009	0.007	0.016	0.123
	4	94.5	0.0009	0.007	0.016	0.123
	5	95.5	0.0006	0.005	0.013	0.111

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Food	Sample No.	Moisture %	Nitrate Nitrogen %	Equivalent to Saltpeter %	Dry Basis: Nitrate Nitrogen %	Dry Basis: Saltpeter %
Potato	1	84.3	0.0024	0.015	0.0152	0.097
	2	80.4	0.002	0.014	0.010	0.071
	3	82.4	0.002	0.014	0.007	0.047
	4	83.4	0.0014	0.0108	0.0084	0.065
	5	80.0	0.0009	0.007	0.0045	0.035
Carrots	1	85.5	0.002	0.016	0.014	0.114
	2	85.5	0.0016	0.012	0.010	0.083
	3	93.2	0.0009	0.007	0.013	0.102
Corn Meal	1	13.3	0.0019	0.014	0.002	0.016
	2	12.9	0.0015	0.012	0.0017	0.013
Sweet Potato	1	70.0	0.0029	0.014	0.0096	0.047
	2	74.5	0.0029	0.014	0.0114	0.055
	3	73.2	0.0009	0.007	0.0033	0.026
	4	73.4	0.0009	0.007	0.0033	0.026
	5	73.8	0.0008	0.006	0.0030	0.022
	6	74.3	0.0006	0.004	0.0023	0.017
Canned Tomatoes	1	94.2	0.0017	0.013	0.029	0.220
	2	95.5	0.0004	0.003	0.009	0.067
Plums	1	86.7	0.0013	0.011	0.010	0.081
	2	77.0	0.0009	0.006	0.004	0.027
	3	88.0	0.0006	0.004	0.003	0.018
	4	75.9	0.0006	0.004	0.002	0.017
Bananas	1	73.8	0.0015	0.011	0.006	0.042
	2	70.9	0.0014	0.0106	0.005	0.035
Apples	1	92.3	0.0013	0.0100	0.017	0.130
	2	90.2	0.0012	0.0089	0.012	0.091
	3	92.8	0.0004	0.003	0.006	0.042
	4	83.2	0.0003	0.002	0.002	0.012
Canned Peas	1	75.6	0.0013	0.0095	0.0053	0.039
	2	73.9	0.0010	0.0072	0.0038	0.028
	3	92.9	none	none	none	none
	4	90.5	"	"	"	"
Sweet Corn	1	79.2	0.001	0.009	0.005	0.043
	2	67.6	0.0007	0.005	0.003	0.020
Rice	1	12.3	0.0013	0.009	0.0015	0.0102
	2	11.9	0.0004	0.0031	0.0005	0.0035
Canteloupe	1	90.6	0.0011	0.008	0.012	0.085
	2	93.1	0.0006	0.0045	0.009	0.065
Parsnip	1	80.0	0.001	0.008	0.005	0.039
	2	78.0	0.0008	0.006	0.0036	0.027
	3	80.1	0.0004	0.003	0.0019	0.015
Orange	1	91.4	0.0009	0.0071	0.0100	0.083
Barley	1	11.2	0.0009	0.0071	0.0010	0.008
"Cream of Wheat"	1	11.9	0.0010	0.0072	0.0013	0.008
Watermelon	1	91.5	0.0009	0.0060	0.0106	0.071
Canned Corn	1	76.1	0.0008	0.006	0.0035	0.025
	2	74.7	none	none	none	none
	3	76.3	"	"	"	"

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Food	Sample No.	Moisture %	Nitrate Nitrogen %	Equivalent to Saltpeter %	Dry Basis: Nitrate Nitrogen %	Dry Basis: Saltpeter %
Peach	1	81.0	0.0007	0.005	0.004	0.026
	2	93.5	0.0005	0.003	0.008	0.046
Oat Meal	1	11.1	0.0005	0.004	0.0006	0.005
	2	11.4	0.0004	0.003	0.0004	0.003
Pear	1	80.3	0.0004	0.003	0.002	0.018
	2	83.4	none	none	none	none
Canned Asparagus	1	94.8	0.0006	0.004	0.0115	0.077
	2	...	none	none	none	none
Crab Apples	1	86.1	0.0004	0.003	0.0028	0.022
	2	85.3	0.0004	0.003	0.0027	0.020
Lemon	1	83.3	0.0004	0.003	0.0028	0.0203
Oats	1	12.3	0.0004	0.003	0.0005	0.004
Grapes	1	75.6	0.0004	0.003	0.002	0.012
	2	...	none	none	none	none
Grape Nuts	1	...	"	"	"	"
	2	...	"	"	"	"
Wheat	1	43.8	"	"	"	"

In the tables the nitrates are calculated as potassium nitrate for two reasons: first, it was desired to have the figures representing the nitrates in vegetables and those in meats on a comparative basis, and second, potassium is the principal metallic constituent of the ash of plants. All analyses were made on the edible portions only.

In order to have a comparison of the quantities of nitrates occurring in vegetables and in cured meats a number of samples of hams and bacons of various brands were analyzed and the results appear in the following tables. It is to be noted that the quantities are of the same order—although the maximum is not so great—as that found in vegetables.

Schönbein and others have found that nitrates appear in small quantities in human urine, and they conclude that their origin is probably drinking water and vegetable food (since fresh meats contain no nitrates) According to Weyl and Citron the quantity of nitrates is smallest with a meat diet and greatest with an exclusively vegetable diet. The average amount is about 42.5 mg. per liter. In several samples of urine the nitrate content was determined and the general conclusions of other investigators confirmed. Nitrates were found normally in cattle urine also, as would be expected of herbivorous animals. It would be of course impossible, although desirable, from determinations made on urine, to ascertain the total quantities of nitrates ingested with the food inasmuch as a large proportion is undoubtedly reduced first to nitrites and then to nitrogen in the digestive tract through the action of denitrifying bacteria according to the equations:

(1) $MNO_3 \rightarrow MNO_2 + O$ and

(2) $NH_4NO_2 \rightarrow 2H_2O + N_2$

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TABLE B.

SALTPETER IN CURED MEATS OF VARIOUS BRANDS AS PURCHASED IN OPEN MARKET.

Product.	Maker	Moisture per cent.	Nitrate Nitrogen per cent.	Equivalent to Saltpeter per cent.	Dry Basis. Nitrate Nitrogen per cent.	Dry Basis. Equivalent to Saltpeter per cent.
Ham	A	66.6	0.014	0.10	0.042	0.30
"	A	67.7	0.001	0.01	0.004	0.03
"	B	65.7	0.003	0.02	0.009	0.06
"	B	66.2	0.003	0.02	0.009	0.06
"	C	59.8	0.024	0.17	0.060	0.42
"	C	66.2	0.009	0.07	0.027	0.21
"	D	63.8	0.032	0.23	0.088	0.64
"	D	63.3	0.032	0.23	0.087	0.63
"	E	64.4	0.032	0.23	0.090	0.65
"	E	65.1	0.038	0.28	0.109	0.80
"	F	65.6	0.014	0.10	0.041	0.29
"	F	66.1	0.007	0.05	0.021	0.15
"	G	63.9	0.005	0.04	0.014	0.11
"	G	62.7	0.009	0.07	0.024	0.19
"	G	64.6	0.003	0.02	0.008	0.06
"	G	58.8	0.017	0.12		
"	H	66.8	0.048	0.34	0.144	1.02
"	H	65.2	0.048	0.34	0.138	1.00
"	H	65.1	0.024	0.17	0.069	0.49
"	H	65.9	0.022	0.16	0.066	0.47
Bacon	A	22.7	0.008	0.06	0.010	0.078
"	B	24.9	0.0007	0.005	0.0009	0.007
"	B	19.8	0.004	0.034	0.005	0.037
"	C	12.0	0.015	0.11	0.017	0.125
"	C	25.0	0.014	0.10	0.019	0.133
"	D	21.2	0.017	0.13	0.022	0.165
"	D	17.2	0.008	0.06	0.010	0.073
"	E	17.7	0.042	0.30	0.051	0.36
"	E	19.2	0.003	0.02	0.004	0.025
"	F	12.2	0.001	0.01	0.002	0.011
"	F	18.3	0.005	0.04	0.006	0.049
"	G	19.8	0.002	0.014	0.002	0.017
"	G	21.8	0.001	0.010	0.0018	0.013
"	G	20.2	0.001	0.01	0.0018	0.013
"	G	20.5	0.001	0.01	0.0018	0.013
"	H	14.4	0.015	0.11	0.018	0.13
"	H	18.2	0.007	0.05	0.009	0.061
"	H	14.9	0.018	0.13	0.021	0.15
"	H	19.8	0.005	0.04	0.006	0.05
Dried Beef	A	62.8	0.010	0.075	0.053	0.20
"	A	59.0	0.021	0.157	0.046	0.35
"	B	52.9	0.034	0.246	0.072	0.52
"	B	56.7	0.030	0.223	0.070	0.51
"	C	61.9	0.020	0.150	0.052	0.39
"	C	56.7	0.028	0.207	0.064	0.48
"	D	60.2	0.027	0.200	0.069	0.50
"	D	65.9	0.020	0.150	0.059	0.43
"	E	66.2	0.024	0.174	0.071	0.51
"	E	63.8	0.025	0.182	0.069	0.50
"	F	54.1	0.017	0.120	0.037	0.26
"	F	60.5	0.009	0.070	0.023	0.18

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In the second equation the presence of ammonium salts is assumed. In spite of our inability to determine from the nitrates of the urine the total quantity ingested, it is interesting to know that nitrates are regularly taken into the system with the food and regularly eliminated by the kidneys, and when we consider that there is present of nitrates in various fresh vegetables, including beets, squash, parsley, turnips, radishes, celery, cabbage. lettuce, cucumbers, spinash, string beans, and egg plant the equivalent or more than the equivalent of the quantity of saltpeter ordinarily present in cured meats, and considering also the relatively small quantity of meat and particularly of salt meat included in the average diet, we must conclude that the average person obtains a larger quantity of nitrates from his vegetable than from his meat foods.

A diet consisting largely of fresh vegetables is not considered injurious and has not been known to cause injury. Yet, it is possible that on such a diet a person, as a vegetarian, might easily consume the equivalent of one to two grams and possibly more, of saltpeter daily.

In the following table a few calculations are made of the quantities of nitrates figured as saltpeter which would be consumed by a person eating the kinds and quantities specified. All of the percentages are taken from the tables. Those samples containing the largest quantities of saltpeter are purposely selected.

Vegetable	Weight consumed grams	Saltpeter %	Weight Saltpeter consumed grams
EXAMPLE NO. 1			
Beets	100	1.327	1.327
EXAMPLE NO. 2			
Egg Plant	100	0.801	2.168
Spinach	200	0.624	
Celery	25	0.476	
EXAMPLE NO. 3			
Radish	25	0.500	1.645
Turnips	200	0.470	
Lettuce	100	0.580	

Even after making a liberal allowance for nitrates extracted by boiling and pouring off the water during the preparation for the table of some of the foods shown, it will be seen that from one to two grams of nitrates figured as saltpeter could easily be consumed. In passing, it should be noted that the quantities of foods assumed to be eaten per 24 hours are moderate for a person on a mixed diet and extremely moderate for a vegetarian.

No case is known of injury traceable to the consumption of saltpeter contained in cured meats and it is known that persons may eat considerable quantities of such meats even for long periods, without injury. In the light of these facts it would seem that saltpeter as used in cured meats must be classed as a harmless substance.

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It has been persistently reported[1] that the sole object in using saltpeter in the curing of meats is for the purpose of maintaining a red color. This is only one of several objects gained in using the substance. That it is an essential curing agent and that a large percentage of sour meats (in the trade sense) would result if its use were discontinued, can not be successfully controverted. While it must be admitted that saltpeter is not an antiseptic in the sense ordinarily understood by this term it appears to protect in some way the nitrogenous tissue against bacterial invasions.

Possibly the most beneficent rôle of saltpeter in the curing of meats is its transformation of what would otherwise, be anaerobic conditions, into aerobic ones in the bacteriologic sense, a full discussion of which is reserved for a later paper. I need only say here that it has been shown that aerobic bacteria will develop in the absence of air if saltpeter is present in the culture medium and that anaerobes refuse to grow in the absence of air and presence of saltpeter[2]. The fact that typical putrefaction (faülnis) is an anaerobic process[3] and that this process can be transformed into an aerobic one by the presence of saltpeter, is a most important point in the curing of meat.

The presence of nitrates in one other food product is of interest. It was anticipated that inasmuch as nitrates are normally ingested and eliminated there was a possibility of their being present in various bodily secretions particularly milk, although it has been reported in the case of milk as in the case of musts and wines that the presence of nitrates indicated watering. We found nitrates present qualitatively and quantitatively in three out of four samples examined, as follows:

Sample No.	Nitrate Nitrogen %	Equivalent to Saltpeter %
1	0.0016	0.012
2	0.0011	0.007
3	0.0009	0.005
4	none	none

Summary.

1. Nitrates are of general occurrence in plants in all stages of growth, and particularly in the early stages.

2. In the mature parts of plants such as ripe seeds and fruits only small quantities of nitrates are found.

[1] Leach, Food Inspection and Analysis p. 173. Rideal, Disinfection and Preservation of Food, p. 148, 409, 417. Mitchell, Flesh Food, p. 107. Ostertag-Wilcox, Handbook of Meat Inspection, p. 803. Wiley, Foods and Their Adulteration, p. 50. Thresh and Porter, Preservatives in Food and Food Examination, p. 166. König, Chemie der menschlichen Nahrungs und Genussmittel, II, p. 518 and 443.

[2] Pakes and Jollyman, J. Chem. Soc. Trans., 1901, 322, 386, 459 and Frankland, Ibid., 1888, 373.

[3] Flugge, Die Mikroorganismen, I, 259. Lehmann and Neumann, Bacteriology, II, p. 88. Kolle und Wasserman, Pathogenen Mikroorganismen I, p. 110. Lafar, Technical Mycology, I, p. 291. Lafar, Handbuch der Technischen Mykologie, Vol. 3, p. 86.

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3. In some cases notable quantities of nitrates remain in the mature plant: instance ripe beets and turnips.

4. The amounts of nitrates found in vegetables are of the same order but rather more in many instances than those found in cured meats.

5. A person on a diet consisting of fresh vegetables, wholly or largely, would consume more nitrates than one on a mixed diet consisting in part of cured meats.

6. As much as the equivalent of from one to two grams of saltpeter daily could be consumed by a person eating fresh vegetables.

7. Inasmuch as a fresh vegetable diet is entirely harmless and as no case of injury from saltpeter in cured meats is on record, saltpeter in the quantities used in cured meats must be classed as a harmless substance.

CHEMICAL LABORATORY OF SWIFT AND CO.
Chicago, Ill.

CORRECTION.

On page 573, lines 5, 6 and 7, of the current volume of the Journal, is found the sentence, "3 cc. of nitric oxide gas mixed with three liters of air will efficiently bleach a kilo of flour." In writing the sentence, I intended to use the word "distinctly" instead of "efficiently," just as I did in the parallel experiment with bromine vapor given at the bottom of the preceding page. S. AVERY.

NEW BOOKS.

THE ELEMENTS OF PHYSICAL CHEMISTRY. BY HARRY C. JONES. Third Edition, Revised and Enlarged. New York, The MacMillan Company, 1907. Price $4, net.

The new edition of this excellent and well known work has been carefully revised. Of the abundant and important material published since the appearance, five years since, of the earlier edition, whatever was fairly within the scope of the book has been incorporated in it, with the result that it has been enlarged by about a seventh part. A goodly number of references to original papers will enable the student to follow a given discussion further than the limits of the text. Naturally, the chapters on Solutions and on Electrochemistry contain the most of the new material, but half of the other chapters show additions.

The new edition well deserves the same commendation and the same welcome as that with which the earlier one was received.

EDWARD W. MORLEY.

ENTWICKELUNGSGESCHICHTE DER CHEMIE. VON A. LADENBURG. Braunschweig, Friederich Vieweg und Sohn, 1907. Price, unbound, 12 marks.

Ladenburg's "Entwickelungsgeschichte der Chemie" is an attempt to trace the development of our present conceptions of chemistry from earlier conceptions, beginning with the time of Lavoisier. By omitting bio-

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graphical details, and by disregarding experiments and opinions which exerted little or no subsequent influence, he has been able to depict the progress of chemical thought for the last hundred years well within the compass of four hundred pages.

The book will be found useful for two different purposes. Its compactness, the clearness of its style, and the wise selection of important facts, well fit the book to the wants of the young student of chemistry who desires to attain some insight into the history of the doctrines and principles of his science. Even for the young student, the copious references to the sources of most of the more important statements will be of value. But these numerous foot notes (there are nearly 1400 references in them) make the volume also serve as a convenient and excellent guide to one who desires to examine more closely the history of some given matter.

Fourteen of these lectures were published in 1869. An edition was published in 1889 to which a fifteenth lecture was added, continuing the history to that date. The present fourth edition contains two more additional lectures, bringing the story down to the year 1906, while the earlier lectures have been carefully revised. The author accordingly, has not spared himself the increased labor of writing the history of matters which are still fluid and mobile and formative. While, as he well says, much in these chapters will need future correction, still, the judgment of a sober-minded, unprejudiced contemporary will have its value.

The chemist who has an intellectual interest in his science and its history cannot afford to be without this book. This is the more true because the work comes nearer to being independent of Kopp than do other brief histories of chemistry; and we all value our Kopp so highly that we would like to have two independent Kopps. EDWARD W. MORLEY.

THE PHYSIOLOGY OF ALIMENTATION. By M. H. FISCHER. New York, John Wiley & Sons; London, Chapman & Hall, Ltd., 1907, pages VIII + 348, figs., 30. Price, $2.00.

It has been the author's purpose to present an outline of the physiology of the digestive tract suitable for the use of students, particularly those who are interested in physiology as related to medicine, and this plan has been admirably carried out. The volume will prove useful also to a wider circle of readers, for it summarizes a large amount of data regarding mechanical phenomena of alimentation, the digestive juices and their constituents, the action of the digestive enzymes, the regulation of secretion of digestive juices, the bacteria of the alimentary tract, and the alimentary tract as an absorptive and an excretory system. Enough is given of the historical side of the questions considered to familiarize the student with the development of the work, but attention is devoted chiefly to setting forth the views which are most generally accepted regard-

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ing digestion and assimilation of food and to summarizing the results of investigations on which these theories are based. The results of the author's own investigations are embodied, as well as a large amount of data from such recent work as that of Cannon, Starling, and Pawlow and his associates, to cite only a few. The index of authors and the detailed index of subjects, in addition to text references to authorities cited, are features which add greatly to the usefulness of the volume.

C. F. LANGWORTHY.

CLEAN WATER AND HOW TO GET IT. By ALLEN HAZEN. Mem. Am. Soc. of C. E. John Wiley & Sons, New York, 1907. Price, $1.50.

In the present day when men from various pursuits are called to serve their city or state in some political office, it is essential that they become familiar with the different departments with which they have to deal. Many technical books may have already been written on the subjects on which they wish to be informed, but books which treat of the practical principles and facts may be wanting. To fill such a need in the department of water supply this book on "Clean Water and How to Get It" was written. It is for beginners, but especially for those who have power to act in a way to bring about better conditions, for those, "who wishing to serve their cities well, can perhaps be aided in doing it by very simple statements as to some matters."

In the first five chapters Mr. Hazen discusses the different sources of supply, their characters and adaptability for use, illustrating his points very clearly by brief but adequate descriptions of specific city works. In a very simple way he explains what hardness, turbidity, and color are, to what due and how best they can be removed. In detail, he describes the mechanical, the slow sand, and intermittent filters, and shows why and how each is good and under what conditions each is best. Then that the book may be complete, he mentions the various parts of the water works, their size according to need for consumption, for manufacturing, for fire service, with a view too, to the pressure required. He deals also with the means of suppression of waste and fair charges, in connection with the cost of construction and maintenance.

The book on the whole is a comprehensive, practical view of the entire subject, giving a general idea as well as specific in some cases, of meeting almost any problem in connection with securing a new supply or improving an old one. It bristles with facts presented in excellent English. From reading it one would be able to see the necessarv requirements, would be able to follow intelligently the methods proposed by an expert and understand why under particular conditions certain devices are best, in short, would be made more competent to fill his position as a man interested, in water works.

R. S. WESTON.

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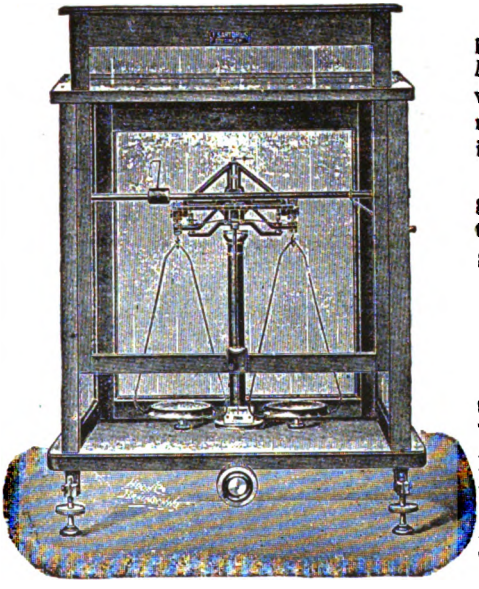
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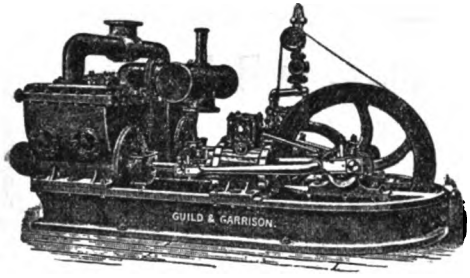
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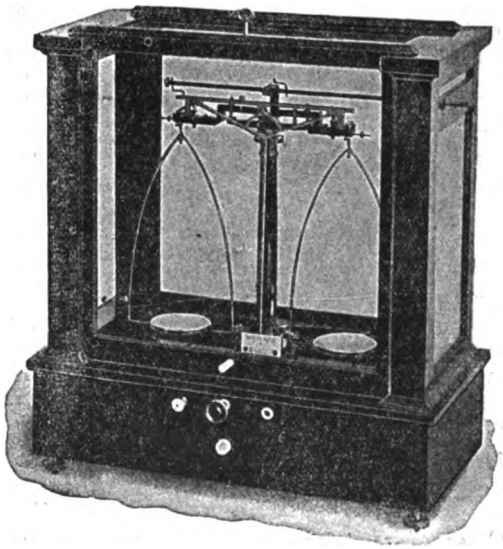
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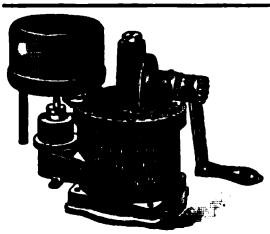
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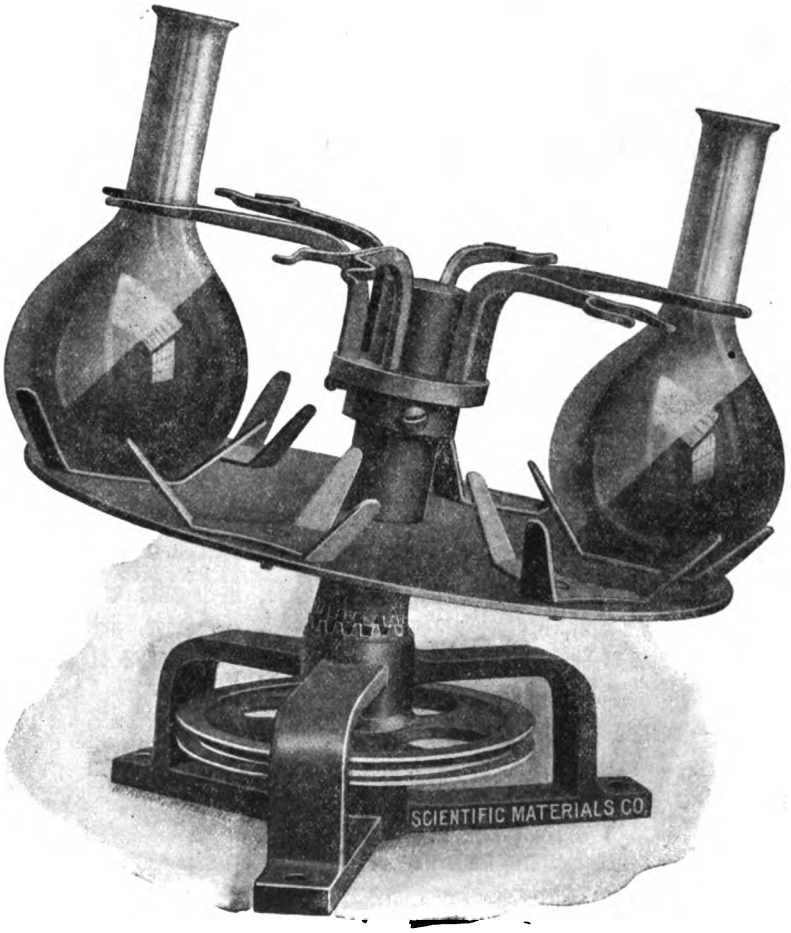
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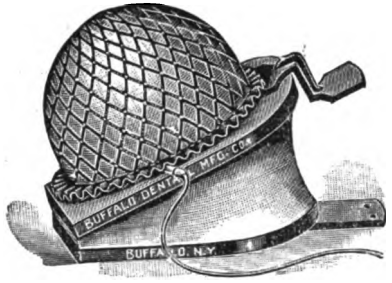
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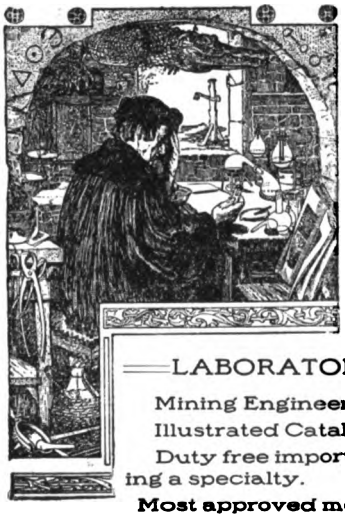
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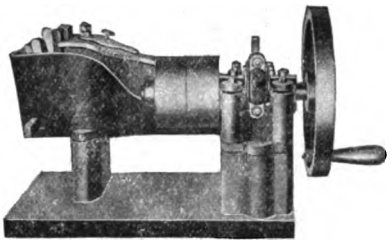
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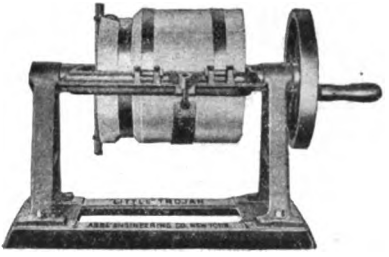


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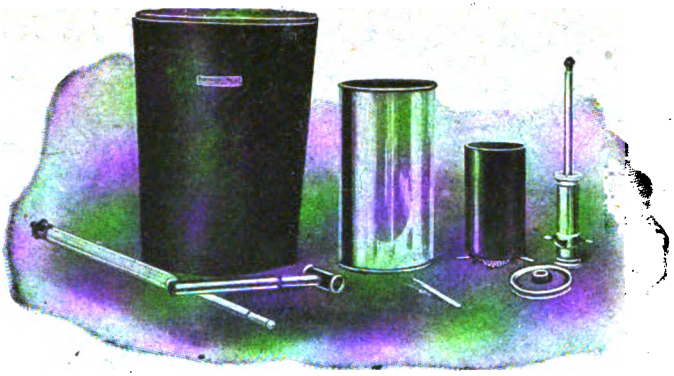
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